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Infrared band gap at the metal-nonmetal transition in NiS

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Optical-reflection spectra have been measured for hexagonal NiS in the energy range 0.01 – 5.0 eV at temperatures both above and below the metal-nonmetal transition near 260 K. Using Kramers-Kronig analysis it is found that the conductivity below 0.1 eV drops on cooling through the transition. Above this energy a peak appears which reaches a maximum near 0.4 eV. The peak is identified with an energy gap which appears in the low-temperature antiferromagnetic phase. The low energy of this peak is contrasted with the predictions of localized-electron models. Comparisons made with recent augmented-plane-wave band calculations which include exchange strongly suggest an itinerant electron model for the transition.

I. INTRODUCTION

The hexagonal form of NiS (α-NiS which has the NiAs structure) is antiferromagnetic at low temperatures. Sparks and Komoto were the first to show that there is a large drop in dc conductivity on cooling through the transition temperature T_t $= 260$ K and entering the antiferromagnetic (AF) phase.[1] White and Mott[2] and also Koehler and White[3] have reviewed this interesting metal-nonmetal transition and conclude that it is a first-order transition and is accompanied by a narrowing and splitting of the nickel *d* bands below 260 K. These authors suggest that, in the low-temperature phase, the material is a semimetal possessing band antiferromagnetism. In the present paper we will refer to the low-temperature phase as the "nonmetallic" or AF phase though we regard the nature of this phase in real α-NiS as unresolved. McWhan *et al.* have studied the pressure dependence of the transition and also the relative motion of the sulfur atoms in the unit cell.[4] Their x-ray results appear to rule out band splittings which occur as a direct result of atom displacements. Briggs *et al.* have measured some of the low-energy phonon and magnon spectra of NiS.[5] They deduce a very high spin-wave velocity, which is consistent with an itinerant model for the AF phase. While many of the earlier experimental studies have measured the jump in resistivity at T_t, there have been no previous optical studies which show what gaps, if any, occur in the NiS energy bands.

It is quite easy to show that, independent of the mechanism of the transition, the large change in dc conductivity (by a factor of from 10 to 150) must be balanced by a change in optical absorption in some spectral region away from $\omega = 0$. This type of argument, based on the sum rule, has been presented before for antiferromagnetic chromium metal.[6,7] For example, an energy gap which opens over some or all of the Fermi surface removes free carriers in these regions from participation in the intraband (dc) conductivity. This reduced participation causes the conductivity drop on cooling through the transition. For photon energies larger than the band gap the same electrons may now undergo transitions to higher-lying empty states and thus give increased absorption at these higher energies.

This paper presents an optical-reflectivity study and analysis of hexagonal NiS. The results show a strong absorption peak near 0.14 which is interpreted in terms of an energy gap that appears at temperatures below T_t. The energy gap is compared with band calculations for the AF phase in NiS.[8] In Secs. II–V we discuss sample preparation (Sec. II), the optical measurement techniques (Sec. III), the data analysis and results (Sec. IV), and finally discussion and comparison with theories of the transition in NiS (Sec. V).

II. SAMPLE PREPARATION AND CHARACTERIZATION

Single crystals of NiS were prepared by sealing the elements in an evacuated quartz tube and heating to 1000 °C. The method has been described previously.[4] Since the hexagonal form of NiS (α-NiS) is stable above approximately 650 °C, the reaction tube is quenched from 750 °C to room temperature to avoid formation of the unwanted millerite phase. This procedure yielded crystals 2 cm long × 8-mm diameter with the *c* axis inclined approximately 30° to the axis of the cylinder. Small samples (1 mm × 0.5 mm × 0.5 mm) were taken from each end of the sample and often from a point near the center to measure the resistance as a function of temperature. The remaining material was cleaved to prepare samples with faces perpendicular to the *c* axis or spark cut along the *c* axis to obtain a large face with the *c* axis lying in the plane. The resistance measurements on almost all samples showed a transition, i.e., an abrupt rise in resistance by a factor of from 2 to 10 on cooling. Well-annealed stoichiometric NiS exhibits the transition at $T_t = 260$ K.[9] The samples used for the present study had transition temperatures in the range 200–230 K. Typically, the resistance test sample which was taken from a region adjacent to the optical sample would show a resistance characteristic which rose from 10% to 90% of the total resistance change in a range of about 10 K.

The samples which had been spark cut were polished using standard optical abrasives in a water slurry on a glass lap. Preliminary optical spectra showed that such a polishing procedure completely removed the optical effects associated with the transition. Apparently the strain or heat associated with the polishing either causes the surface material to revert to millerite or depresses T_t considerably below the range of temperatures studied. It was found that an electroetch[10] which removed several microns of material exposed a surface which did show the optical effects at the transition similar to those observed on a cleaved face. The electroetch procedure was used on all samples for which spectra with the electric field (E) polarized parallel to the c axis were measured and in one case was also used for $\vec{E} \perp \vec{c}$ for comparison with a spectrum taken on a cleaved surface.

In order to measure the reflectivity in an absolute manner an aluminum reference film was evaporated on half of the surface under investigation. While this film adhered well at room temperature, it usually cracked and peeled on passing through the transition. In a few cases it cracked following cracks in the sample which could be observed *in situ* during the low-temperature experiment. Since the samples cracked badly, occasionally even falling to pieces inside the cryostat, it was extremely difficult to normalize the reflectivity for spectra taken below T_t.

III. OPTICAL MEASUREMENTS

Reflectivity spectra were measured in three energy ranges using different techniques. Most of the work was done in the range 0.04–2.0 eV using a double-pass prism spectrometer together with methods which have been described in earlier publications.[11] The energy gap which appears in the AF phase occurs in this energy range. Spectra were measured at 80, 200, and 300 K using an evacuated Dewar with movable cold finger and suitable optical windows. Because of the difficulty mentioned above of normalizing the reflectivity data when the sample has cracked, several extra measurements were made in a very limited energy range near 0.1 eV in an attempt to enter the low-temperature phase and maintain the reference aluminum film on one side of the sample area intact. These attempts were not completely satisfactory and the normalization of the low-temperature reflectivity data is felt to be uncertain by about ±4% on an absolute scale compared with an uncertainty of ±1% for the 300-K data. Figure 1 shows $\vec{E} \perp \vec{c}$ spectra in this range.

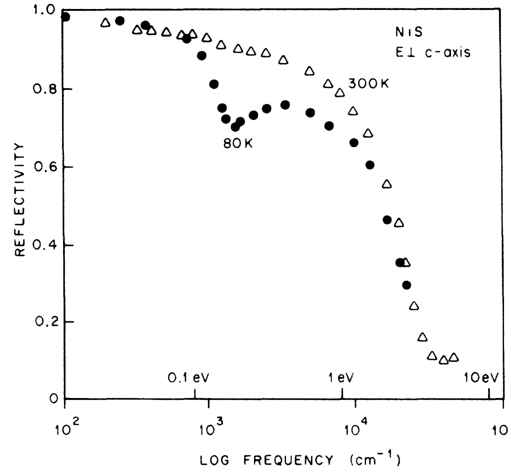

FIG. 1. Polarized reflectivity spectra for a sample of NiS taken above and below the transition temperature $T_t = 230$ K. A prominent dip near 0.14 eV appears at low temperatures. There is also additional weak structure near 4.5 eV at both temperatures which is not shown here.

Additional reflectivity measurements were made in the range ~3 meV to 45 meV using a far-infrared Michelson interferometer. Measurements were made at 300 K and in the AF phase at 80 K for one polarization. The data are shown in Fig. 2. Spectra were measured in the range 2–5.2 eV using the prism spectrometer converted to single-pass operation and a LiF prism. In both the very low-energy range and this latter high-energy range no careful attempts were made to obtain absolute reflectivity since we were principally interested in searching for new structure.

Figure 1 shows that at room temperature the metallic phase shows a fairly high reflectivity below 1 eV typical of a d-band metal. At 80 K a pronounced dip appears in the spectrum near 0.14 eV. This is the important piece of new structure. To obtain measurements of anisotropy, spectra were taken for one sample which contained the c axis in the plane of the reflecting face. This sample was measured at room temperature for $\vec{E} \parallel \vec{c}$ and $\vec{E} \perp \vec{c}$ by using a rotatable polarizer. The sample was then cooled to the low-temperature phase and remeasured for the two polarizations. The spectra were very similar to those shown in Fig. 1. To obtain good relative values the measurements were all completed within an hour while maintaining the temperature constant to within 1 or 2 K. The small differences between the two polarizations are discussed in Sec. IV.

IV. DATA ANALYSIS AND RESULTS

A. Kramers-Kronig analysis

At room temperature the samples which had been polished and then electroetched always showed the highest reflectivity. The reflectivity was measured by comparing the reflected signal from the sample with that from a freshly evaporated aluminum surface on part of the sample as has been discussed previously. Cleaved samples showed a somewhat lower reflectivity (a few percent) probably because of the many random steps on the surface resulting from the cleaving process. Spectra for these samples were also measured relative to an Al mirror which was mounted next to the sample and were finally scaled upwards to agree with the reflectivity measured on the best electroetched surface. To complete the reflectivity spectra the data were extrapolated below 300 cm^{-1} by adding points generally following the monotonic rise shown in Fig. 2. Above 2 eV the data were smoothly extrapolated to asymptotically approach a constant value of from 0.25 to 0.30. Figure 3 shows a Kramers-Kronig analysis of the data in Fig. 1 using the extrapolation procedure described above. Tests using various extrapolation procedures show that the curves in Fig. 3 may be floated up and down to some extent depending on the method used but the prominent features of the curves remained invariant. In particular the peak (dashed curve) near 0.4 eV retains its shape and energy location. The dip in reflectivity in the insulating phase gives on analysis this strong peak in the optical conductivity. The threshold is at 0.14 ± 0.02 eV and the conductivity reaches a maximum at 0.4 eV. This is the gap absorption associated with the nonmetallic phase.

Figure 4 shows the results of analyzing the an-

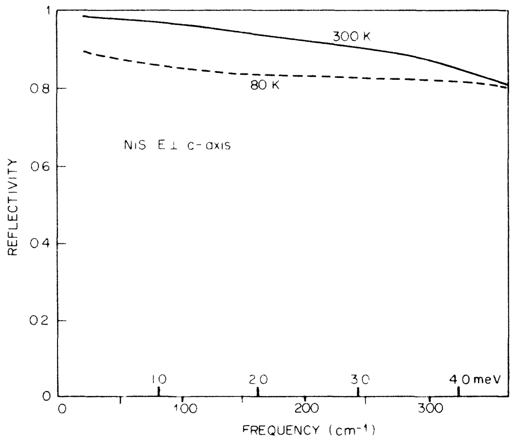

FIG. 2. Far-infrared reflectivity of NiS. The 80-K data have a rather large uncertainty in their normalization; they has been chosen to equal the 300-K reflectivity near 350 cm^{-1}.

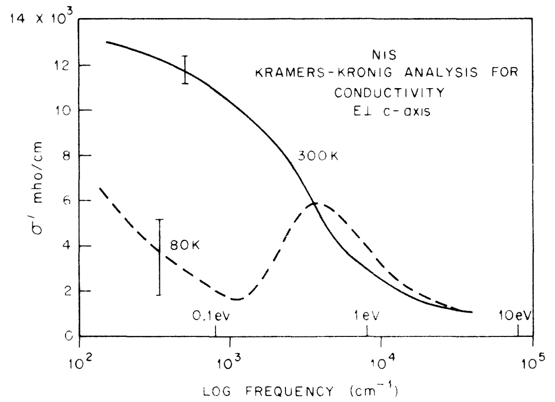

FIG. 3. Real part of the conductivity obtained by a Kramers-Kronig analysis of the data of Fig. 1. Extrapolation of the data to zero and infinite frequency has been carried out as described in the text. The uncertainty bars refer to the entire curves—they may be floated up or down almost rigidly. These uncertainties are estimated from consideration of various extrapolation procedures and from consideration of the reflectivity differences of various NiS samples.

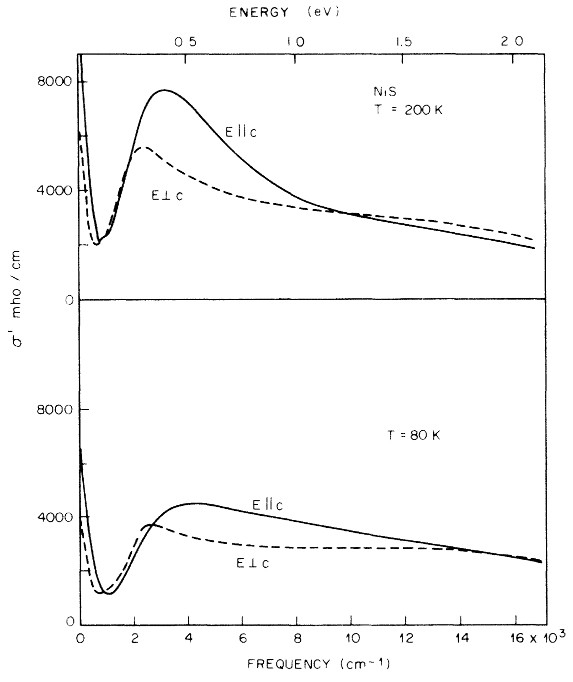

FIG. 4. Conductivity spectra obtained for one sample measured at two temperatures and for two polarizations. The absorption peaks appear much sharper just below the transition at 200 K.

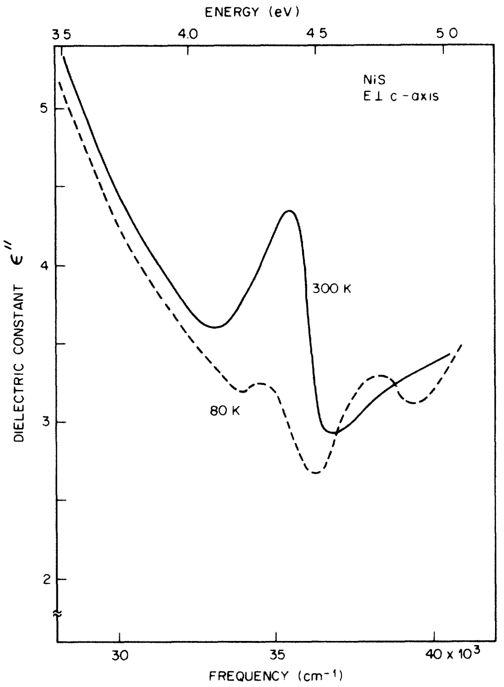

FIG. 5. Imaginary part of the dielectric constant ϵ'' obtained by Kramers-Kronig analysis of the reflectivity data in the visible and ultraviolet regions. The reflectivity data (not shown) have a spectral dependence of roughly the same form as ϵ''. Note the reversion of the 300-K peak into two peaks separated by approximately 0.5 eV at 80 K.

isotropy data. The figure shows that both the absorption edge and peak occur at a lower energy for $\vec{E} \perp \vec{c}$. The edge also appears to be slightly steeper at 200 K compared with the 80-K result.

A separate Kramers-Kronig analysis was carried out on the high-energy reflectivity spectra. Figure 5 shows the imaginary part of the dielectric constant ϵ''. The figure shows that the single-peak structure at 300 K is replaced by two peaks split by approximately 0.5 eV at 80 K. The peak positions shown in Fig. 5 were obtained consistently for three samples, however, their strengths and shapes varied considerably and the final rise in ϵ'' is quite uncertain since it depends critically on the form assumed for the high-energy extrapolation of the reflectivity.

B. Nature of energy-gap absorption

Figure 6 compares the absorption peak in NiS with the energy-gap absorption observed in chromium[7] and in NiO.[12] On cooling through 312 K, Cr undergoes a metal-nonmetal transition in the sense that approximately $\frac{1}{3}$ of the high-temperature Fermi surface is removed by interactions among the itinerant electrons. Cr is the best-known example of an itinerant antiferromagnet. NiO is a d^8 material similar to NiS. However, both above and below its Neél temperature (523 K) it is an insulator and represents a striking example of a material whose insulating properties cannot be explained using a conventional band model.[13] We first wish to establish that the peak in NiS results from electronic excitations across an energy gap. To support this conclusion we examine two potential sources of absorption which could appear in this energy region. In the insulating phase we might expect infrared-active phonons to contribute to the absorption. These may be ruled out for two reasons. First, the peak energy (0.4 eV) is five times higher than the energy where we would expect infrared optic-phonon modes. The second (and stronger) argument is that the integrated strength of any of the peaks shown in Fig. 4 is at least 200 times stronger than a typical infrared phonon. A second possibility is that the absorption peak is connected with spin waves. Briggs *et al.*[5] have shown that the zone-center spin-wave gap is 12.6 meV. This energy is much too low to be associated with the present absorption peak and apparently the mode is too weak to show in the low-frequency spectra of Fig. 2. The locations of various zone-edge spin-wave energies are not known. We note that a photon-absorption process must be connected with the excitation of two spin waves with the largest contribution coming from branches near the zone edge. Such absorption in MnF_2[14] shows a peak which is 10^4 times weaker than the peaks shown in Fig. 4. On this basis we assume that the NiS peak is not associated with spin waves. We therefore associate the absorption peak in NiS with electronic transitions across a gap and note that the peaks are slightly stronger for $\vec{E} \parallel \vec{c}$ which correlates with the larger conductivity in the metallic phase for $\vec{E} \parallel \vec{c}$ and the larger conductivity change on passing through the transition for this polarization.

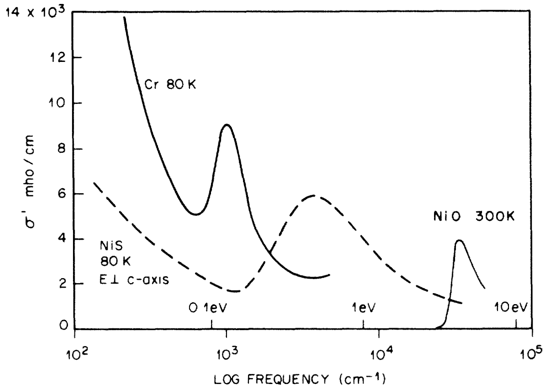

FIG. 6. Comparison of the absorption peaks in Cr, NiO, and NiS in their AF phases.

C. Absorption strength and sum rule

We now apply the sum rule to NiS to correlate the behavior above and below the transition temperature T_t. This procedure has fairly large uncertainties since the dc conductivity is rather uncertain. Table I shows the results of three recent investigations of the conductivity. In the present work we have measured only the resistance of the samples which includes contact and lead resistance. For the present comparisons we arbitrarily adopt the values from Ref. c in the table since those samples were grown under the same conditions as the samples used in the optical study. Figure 3 shows that the 300-K data would be consistent with our adopted value of 14.3×10^3 mho/cm for $\sigma_{dc}(300\text{ K})$. Choosing 2000 cm^{-1} as a cut-off frequency and smoothly extrapolating the 300-K data of Fig. 3 to $\sigma_{dc}=14.3\times10^3$, we find

$$\begin{array}{l}\text{Intraband sum rule}\\ \text{contribution at 300 K}\end{array} \simeq \int_0^{2000\text{ cm}^{-1}} \sigma'_\perp d\nu = 22\times10^6\text{ mho/cm}^2 \qquad (1)$$

for the real part of the conductivity component perpendicular to the *c* axis. Table I shows that the dc conductivity drops at least a factor of 7 so that substantially all of the intraband conductivity of Eq. (1) is removed on cooling to 80 K. This contribution must reappear somewhere else in the optical spectrum and we now test the magnitude of the absorption in the 80-K peak at 0.14 eV. Using the data of Fig. 4, we find

$$\begin{array}{l}\text{Absorption peak sum}\\ \text{rule contribution at 80 K}\end{array} \simeq \int_{2000\text{ cm}^{-1}}^{10\,000\text{ cm}^{-1}} \sigma'_\perp d\nu = 24\times10^6\text{ mho/cm}^2 \; . \qquad (2)$$

This result is probably somewhat too large because of failure to subtract a background from the 80-K conductivity curve.[7] The approximate agreement of the integrated conductivity given by Eqs. (1) and (2) show that the low-temperature peak does contain most or all of the contribution lost from the intraband conductivity on cooling through the transition. This result shows that from the point of view of the conductivity sum rule the important changes at the transition temperature in NiS are as follows. Above the transition temperature the conductivity appears metallic with most of the intraband contribution lying below 0.5 eV. On cooling through the transition there is a substantial rearrangement of the energy bands near the Fermi energy including the appearance of an energy gap. This rearrangement of the bands causes the intraband conductivity to drop to a rather low value. The samples used in the present study do not exhibit insulating behavior, but the conductivity does drop to a small fraction of the high-temperature value. It may be that samples prepared in a different manner would show insulating behavior well below T_t.

TABLE I. Typical dc conductivities above and below the transition in α-NiS.

Sample	Transition temperature (K)	$T=300$ K metal (mho/cm)	$T=80$ K Insulator (mho/cm)
4–7[a]	200	$\sigma_\perp=10.5\times10^3$	1.5×10^3
3–10[a]	225	$\sigma_\perp=3.2\times10^3$	0.27×10^3
Ref. b	210	$\sigma_\parallel=29\times10^3$	0.30×10^3
		$\sigma_\perp=17\times10^3$	0.40×10^3
Ref. c	230	$\sigma_\perp=14.3\times10^3$	1.9×10^3

[a] Reference 15.
[b] Reference 3.
[c] Measured under 2.5-kbar pressure, Ref. 4.

The optical conductivity peak below T_t does not show a unique value for the energy gap. The data suggest that either the gap is indirect with a value near 0.14 eV with poor stoichiometry (defects) and phonons allowing transitions above this energy or there is a spread in gap values over the Fermi surface so that the optical data can only define an average gap somewhere in the range 0.14–0.4 eV.

V. DISCUSSION

Figure 6 shows the absorption peak in chromium associated with the spin-density-wave energy gap compared with the measured absorption in NiS. Chromium is an itinerant antiferromagnet and a modified weak-coupling theory[6] based on a two-band model of the itinerant electrons predicts

$$\hbar\omega_g = 5.2kT_t \; , \qquad (3)$$

where $\hbar\omega_g$ is the energy gap, k is Boltzmann's constant, and T_t in chromium is the Néel temperature. If we insert the gap observed for NiS (0.14–0.4 eV) into Eq. (3), we would predict T_t in the range 310–890 K. While the latter temperature is close to an estimate of the extrapolated Neél temperature,[2] it is evident that Eq. (3) does not predict the gap correctly. This failure is probably connected with the fact that the transition in NiS is strongly first order compared with the nearly second-order transition in Cr. In addition, the optical experiments on Cr showed that the absorption peak was rather broad and ill-defined just below the transition temperature but became considerably sharper on cooling to 80 K. In Cr this broadening of the absorption near the transition temperature is caused by the depairing effects associated with electron-phonon coupling.[6] Figure 4 shows that in NiS the absorption peak is sharpest immediately below the transition and becomes broader on cooling. This effect is not understood. The above points show that a two-band weak-coupling model as used for

Cr would have to be modified to predict the gap formation in NiS.

We next make comparisons with certain Hubbard-model calculations for the energy gap. In a sense this comparison involves going to the opposite extreme from the Cr comparison. This model is thought to be applicable to NiO. The important parameter of the Hubbard model is the intra-atomic Coulomb interaction U. Brinkman and Rice[16] have shown that in the atomic limit (i.e., large U), the absorption spectrum consists of a peak of approximately Gaussian shape centered at energy U and with width approximately equal to the bandwidth of the noninteracting bands. Using the estimate[2] $U = 2$ eV, we find that the predicted absorption peak occurs a factor of 5 too high in energy. The width of the absorption is also too large for consistency with the experiment since we believe the d-electron bandwidth to be approximately 2–3 eV.

Wilson[17] has made a study of the metal-insulator transition in certain sulfides. Using arguments based on the trends observed in related series of compounds he suggests that NiS_2 is a Mott insulator with a gap of 0.4 eV between the spin-split components of the e_g band. An estimate based on the increased d-d overlap on passing from NiS_2 to NiS suggests that this gap must decrease significantly[18] which would put it in rough accord with our observed gap.

Certain arguments concerning the strength of the gap absorption may also be related to the Mott-Hubbard model of the insulating phase. In Eq. (2) above, an integral over the gap absorption was performed. It is probably worth noting that arguments depending on the integrated absorption remain valid even if the gap is not simply related to the one-electron band structure discussed above but is connected with many-body effects as envisaged in the Mott-Hubbard transition. We now perform a different integral over the gap absorption to evaluate the contribution of the gap to the dielectric constant at energies below 0.1 eV. If we denote the imaginary part of the dielectric constant connected with the gap absorption by ϵ'', then the contribution $\Delta\epsilon$ to the low-frequency dielectric constant is given by

$$\Delta\epsilon = \frac{2}{\pi}\int_0^\infty \epsilon''\,d\nu/\nu \approx \int_{1000\ \mathrm{cm}^{-1}}^{20\,000\ \mathrm{cm}^{-1}} \epsilon''(T = 80\ \mathrm{K})\,d\nu/\nu\ . \qquad (4)$$

Taking the data of Fig. 4 for $\vec{E} \parallel \vec{c}$ at 80 K and converting the conductivity σ' to dielectric constant ϵ'', we obtain the value 116 for the contribution to the dielectric constant. This rather large dielectric contribution has two consequences. First, it makes extremely difficult the resolution of the question of whether NiS is a semimetal or a semiconductor in the low-temperature phase. Any impurities or defects associated with the poor stoichiometry can give large contributions to the electrical conductivity in a material with such a large dielectric constant. Figure 2 shows that the samples used for the present study exhibited metallic reflectivity at low energies. There is no direct way of deciding whether this reflectivity is associated with overlapping bands or with semiconduction in one band induced by defects acting as donors or acceptors. The Kramers-Kronig analysis of the reflectivity does not show a well-defined Drude form for the conductivity. The resolution of this question of semimetal versus semiconductor may well depend on the discovery of crystal-growth methods which result in far better stoichiometry than has yet been achieved.

A second consequence of the large effect of the gap on the dielectric constant is a self-consistent enhancement of the gap formation on the basis of the Mott picture of the transition. As NiS makes the transition from metal to insulator, the sum rule limits the integrated conductivity σ' to the magnitude given by Eq. (1) above. The contribution of this absorption to $\Delta\epsilon$ is not thus limited; it varies considerably depending on the energies where the principal absorption occurs. If we picture a very small gap beginning to open up as the material makes the transition to the insulating phase, then the contribution to $\Delta\epsilon$ is much larger than the value 116 above. As the gap opens, this contribution decreases because of the frequency factor $1/\omega^2$ which must be included in changing from the sum-rule integral of Eq. (1) to the dielectric-constant integral of Eq. (4).

In its simplest form the Mott criterion for the formation of an insulating phase is that the intra-atomic energy U must be larger than a certain critical quantity. U is given by

$$U = e^2/\epsilon\bar{r}\ , \qquad (5)$$

where ϵ is the dielectric constant and $\bar{r}$ an average charge separation connected with the Coulomb interaction of two d-orbital charge densities on one atomic site. The ϵ to be used in Eq. (5) is probably not directly the long-wave low-frequency $\Delta\epsilon$ of Eq. (4); we expect, however, that $\Delta\epsilon$ does contain some direct contributions to ϵ. As the energy gap increases and $\Delta\epsilon$ decreases, we note that U should increase, and this further favors or reinforces the insulating phase and widens the gap. This argument appears to be appropriate to NiO where the gap is about 4 eV and $\Delta\epsilon$ has a value of about 1.2. The small gap observed in NiS is rather surprising in view of this potential driving force towards a large gap. It suggests that a picture based on the localized limit is not appropriate in NiS.

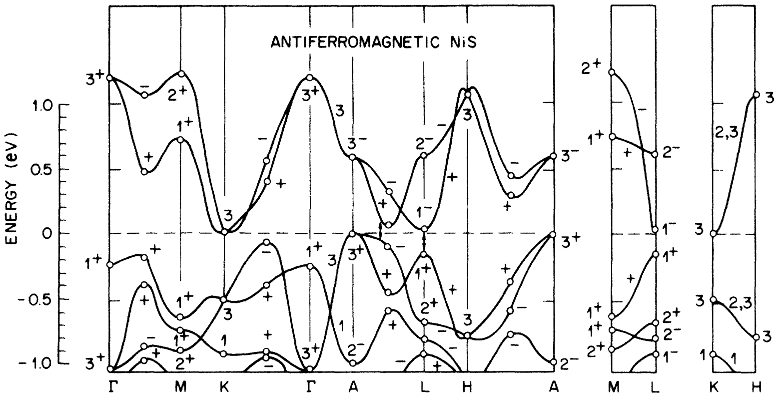

FIG. 7. Band structure of NiS in the antiferromagnetic phase calculated by Mattheiss. The two smallest direct gaps appear between the A and L symmetry points and are marked by arrows.

Finally, we make comparisons with recent computations of the band structure of NiS by Mattheiss.[8] His calculation simulates the antiferromagnetism in NiS by adding a superlattice component to the potentials used in the paramagnetic phase. A constant positive potential $+V_s$ is added within the APW sphere around one Ni atom and a constant negative potential $-V_s$ within the APW sphere around the second Ni atom. These two Ni atoms within the primitive unit cell lie along the c axis and are spaced $\frac{1}{2}c$ apart. The potential which has been added makes the two atoms inequivalent, where previously they were connected by a screw translation of $\frac{1}{2}c$ along the c axis. Figure 7 shows some of the band structure for antiferromagnetic NiS with V_s chosen to be 0.54 eV. From Fig. 7 we note that V_s induces gaps at the Fermi energy (dashed line), with the smallest direct gaps lying along the AL symmetry line. For the actual value of V_s used in the calculation the gaps are 0.15 eV halfway between A and L and 0.19 eV at L. These values are in reasonable agreement with our measured threshold near 0.14 eV.

We now consider the optical-selection rules in the ALH plane. Inversion is an allowed operation at the A and L symmetry point so that parity is a good quantum number. The transitions across the smallest gaps at A and L correspond to a parity change and are therefore allowed. A consideration of the character tables shows that these lowest transitions are allowed for $\vec{E} \parallel \vec{c}$ and $\vec{E} \perp \vec{c}$ at A and H and for $\vec{E} \perp \vec{c}$ at L. We generally expect no selection-rule restrictions at nearby points of lower symmetry. The observation (Fig. 4) of a strong absorption peak with similar strengths for $\vec{E} \parallel \vec{c}$ and $\vec{E} \perp \vec{c}$ is consistent with these results.

The reflectivity study in the high-energy range (Fig. 5) showed major peaks near 4.5 eV. Examining the NiS band structure of Ref. 8 (Figs. 2 and 3) we find that this is the expected energy range for S(3p) – Ni(3d) transitions at many of the points in the Brillouin zone. The band calculation shows the empty Ni(4s – 4p) bands about 4.5 eV above the Fermi level so that 3d to 4s – 4p transitions may also be the source of the observed peaks.

Figure 8 shows schematic representations of band splittings and gaps associated with the metal-nonmetal transition in NiS. The schematic band structure in the low-temperature phase proposed by White and Mott is shown in Fig. 8(a). These authors suggest that a Hubbard gap crosses the Fermi level E_F in the $\Gamma - M$ symmetry direction, causing semimetallic behavior. Koehler and White[3] have suggested a density-of-states model for NiS for temperatures above and below the transition which is shown in Fig. 8(b). The bands that they label as e_g become narrowed and split for $T < T_t$. In addition, a separate band which they label as 3p remains undisturbed and contributes to the intraband conductivity. It is apparent from these schematic band pictures that neither causes complete insulating behavior since they both leave a

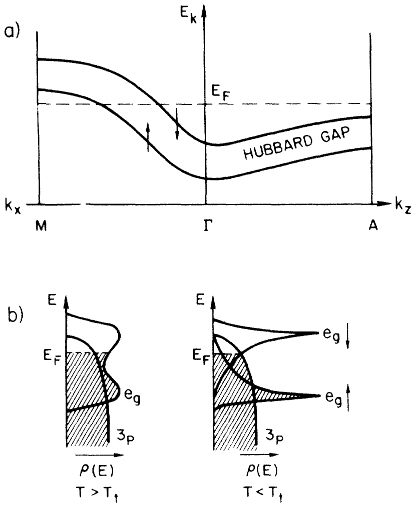

FIG. 8. (a) Bands and splittings along the k_x and k_z directions in NiS proposed by White and Mott. (b) Density-of-states models of Koehler and White.

considerable region of band states near the Fermi energy. The results of the present optical study, showing a low-energy gap, combined with the band calculation of Mattheiss, suggest that Fig. 8(b) gives a better representation of NiS. Except for the 0.14-eV gap the changes on a larger energy scale appear rather minor. This latter result is consistent with recent x-ray photoelectron spectra.[19] These spectra made with a resolution of 1.3 eV show no changes in the density of states of NiS on passing through the transition.

In summary we note that comparisons with the Hubbard model show that NiS is far removed from the localized limit where the intra-atomic energy U is the controlling parameter. In this connection we emphasize again the contrast with NiO which has a gap ten times as large as NiS. A model based on one-electron band calculations appears to be entirely appropriate for describing the low-energy gap which has been observed though the detailed energetics which control the transition have yet to be elucidated.

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