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Article *in* Journal of the Physical Society of Japan · February 1990

DOI: 10.1143/JPSJ.59.435

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Journal of the Physical Society of Japan
Vol. 59, No. 2, February, 1990, pp. 435–438

LETTERS

Reflectivity Spectra in Single Crystals of Cr_3Te_4, Cr_2Te_3 and Cr_2Se_3 between 0.3 and 23 eV

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(Received October 27, 1989)

Single crystals of Cr_3Te_4, Cr_2Te_3 and Cr_2Se_3 were grown by the chemical vapor transport technique. Reflectivity spectra of these crystals were measured for photon energies between 0.3 and 23 eV. Real and imaginary parts of optical conductivity were calculated from reflectivity spectra. The spectra of the real part of conductivity in chromium tellurides were compared with the joint density of states curves evaluated from the energy bands calculated by Dijkstra. Fairly good agreement was obtained between experiment and calculation for Cr_3Te_4.

[reflectivity spectrum, synchrotron radiation, Cr_3Te_4, Cr_2Te_3, Cr_2Se_3, nickel arsenide structure, optical conductivity, joint density of states]

We have been studying optical reflectivity spectra on various kinds of transition metal chalcogenides including pyrite-type compounds,[1,2] chalcopyrite[3] and nickel arsenide-type selenides[4] to elucidate the electronic structures of these crystals. Through these studies, we have come to the conclusion that most of the optical properties of transition metal chalcogenides can be explained in terms of the joint density of states evaluated from the band calculation. In this paper we report optical reflectivity studies in single crystals of the chromium chalcogenides, Cr_3Te_4, Cr_2Te_3 and Cr_2Se_3.

The crystal structures of these chalcogenides are derived from the nickel arsenide structure showing several types of superstructures due to the ordering of the cation vacancies.[5] These compounds are known to show diverse magnetic and electrical properties;[5] Cr_3Te_4 is ferromagnetic with the Curie temperature of 325 K. It also shows an order-to-order magnetic transition around 80 K, below which it shows canted antiferromagnetic properties. Electrically, this compound behaves like a metal. Cr_2Te_3 is also a ferromagnet with the Curie temperature of 182 K. Its electrical conductivity is also metallic. Contrary to the above tellurides, Cr_2Se_3 is an antiferromagnetic semiconductor with the Néel temperature of 43 K. Therefore, of these three compounds, Cr_3Te_4 is only one that shows a macroscopic magnetic moment at room temperature. Magnetooptical spectra were measured in this compound for photon energies between 0.5 and 3 eV, which showed a peak at 1.3 eV with the maximum Kerr rotation of 7 minutes of arc at room temperature. Details have been published elsewhere.[6,7]

Single crystals of Cr_3Te_4, Cr_2Te_3 and Cr_2Se_3 were grown by chemical transport technique, using iodine as the transporting agent. The crystals obtained had a platelet shape with dominant facets of the (001) crystal plane. All of these crystals showed a metallic luster.

Near-normal reflectivity spectra of these compounds were measured on the major plane (001) of crystals for photon energies between 0.3 and 23 eV. Reflectivity below 4 eV was measured at the Tokyo University of Agriculture and Technology using the same reflectivity equipment as was used for the studies in pyrite-type compounds.[2] For

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energies higher than 4 eV, we employed the VUV light from the storage ring at the Synchrotron Radiation Laboratory, Institute for Solid State Physics, University of Tokyo. Ideally speaking, VUV reflectivity spectra should be measured on well-defined cleaved surfaces. However, our crystals were too small to obtain smooth and specular surfaces by cleaving. Moreover, cleaving does not neccessarily provide a clean surface when crystals contain inner voids, which is often the case in crystals grown by chemical transport. Samples were slightly (for a few minutes) etched with concentrated chloric acid and rinsed with deionized water for ten minutes prior to setting into the vacuum chamber. No other precautions were taken for the surface conditions, since any treatment such as sputtering would introduce some other effect on the sample surface. Spectra of the low energy region and the high energy region were connected and calibrated at the visible wavelengths using the optical constants evaluated by a spectroscopic ellipsometer.

Figure 1 illustrates reflectivity spectra in these crystals at room temperature. These three spectra have a common feature in the high energy region, while different structures are seen in the low energy part of these spectra. Real and imaginary parts of the conductivity spectra were then calculated by the Kramers-Kronig analysis of the reflectivity spectra with extrapolation beyond experimental range as follows. Below the lowest energy limit of measurement, reflectivity was assumed to follow the Drude formula in metallic compounds (chromium tellurides), whereas it was assumed constant in semiconducting compounds (chromium selenide). Parameters for the Drude formula were determined so that the real part of the conductivity at the low energy limit was consistent with the dc conductivity. For energies above 23 eV reflectivity spectra were extrapolated using the E^{-4}-formula. The obtained spectra of σ' (real part of the conductivity) are plotted in Fig. 2 by solid, dashed and dot-dashed lines for Cr_3Te_4, Cr_2Te_3 and Cr_2Se_3, respectively.

Recently, Dijkstra calculated energy band structures in various chromium chalcogenides by means of ASW technique.[8] According to

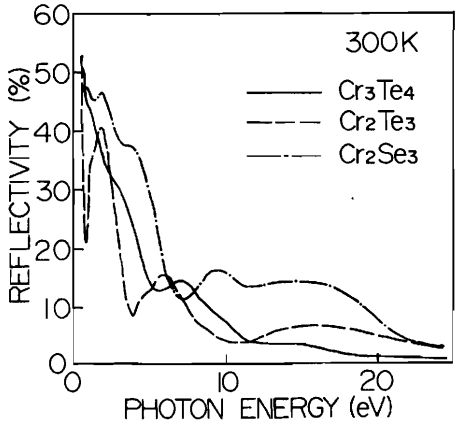

Fig. 1. Reflectivity spectra in Cr_3Te_4 (solid curve), Cr_2Te_3 (dotted curve) and Cr_2Se_3 (dot-dashed curve) at room temperature.

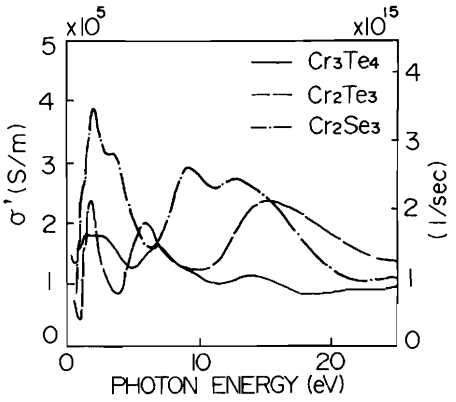

Fig. 2. Spectra of the real part of conductivity in Cr_3Te_4 (solid curve), Cr_2Te_3 (dotted curve) and Cr_2Se_3 (dot-dashed curve) obtained by the Kramers-Kronig analysis of the reflectivity spectra.

his result, the band structure varies depending on the number of vacant metal sites in the NiAs structure. We reproduced the DOS curves he calculated for ferromagnetic Cr_3Te_4 and Cr_2Te_3 in Figs. 3(a) and 3(b), respectively.

From the reported DOS spectra, we made a rough estimate of joint density of states (JDOS) in these materials by applying a simple convolution integral for each spin band. JDOS spectra for both spins were added together and then divided by the photon energy to compare with the experimentally obtained conductivity spectra. The calculated spectra are illustrated by dashed curves in Figs. 4(a) and 4(b) for Cr_3Te_4 and Cr_2Te_3, re-

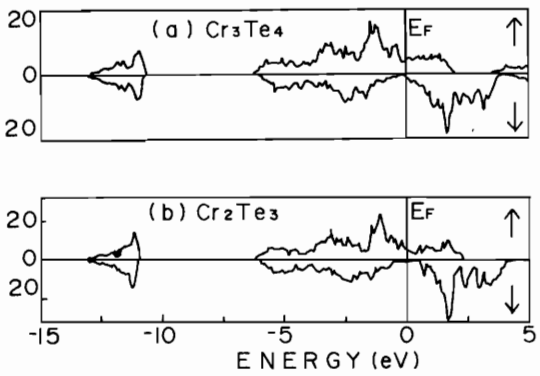

Fig. 3. Calculated density-of-state (DOS) curves in (a) Cr_3Te_4, (b) Cr_2Te_3 reported by Dijkstra.[8]

spectively. For the sake of comparison, the experimental conductivity spectra are also plotted by solid curves in Fig. 4.

In Fig. 4(a) we find a striking agreement of lineshapes between the experiment and the calculation for the energy region 0.5–4 eV in the conductivity spectrum of Cr_3Te_4. The structures a, b and c marked in the experimental spectrum seem to correspond to a′, b′ and c′ in the calculated spectrum.

It is found from these analyses that these structures result from two contributions; one (a′ and b′) is due to the transition from the occupied high-DOS states just below the Fermi level having the chromium 3d character to the empty states above the Fermi level derived from tellurium 5p orbitals in the majority spin band, while the other (c′) is due to the transition from the occupied 5p states of tellurium to the empty 3d states above the Fermi level in the minority spin band. The 3d states in the majority band and those in the minority band are split by the exchange interaction. The hump f around 14 eV seen in the experimental spectrum corresponds to the calculated spectral structure f′ corresponding to the transition from the 3s level of chromium to the empty states above the Fermi level.

On the other hand, no corresponding structures are found in the calculated JDOS curve for the 7 eV peak d observed in the experimental spectrum of Cr_3Te_4. This may result from the lack of higher conduction states located more than 5 eV above the Fermi level in the reported DOS curve of Dijkstra. This fact clearly indicates that this structure can be related to the transition from the occupied states below the Fermi level to the higher-lying conduction bands.

The situation in the Cr_2Te_3 is somewhat different, as seen in Fig. 4(b). Agreement between the experiment and the calculation is rather poor for the low energy peak. A narrow absorption band around 2 eV with the bandwidth of 1 eV exists in the experimental spectrum. By contrast, the calculated JDOS curve does not show such a sharp peak but shows a

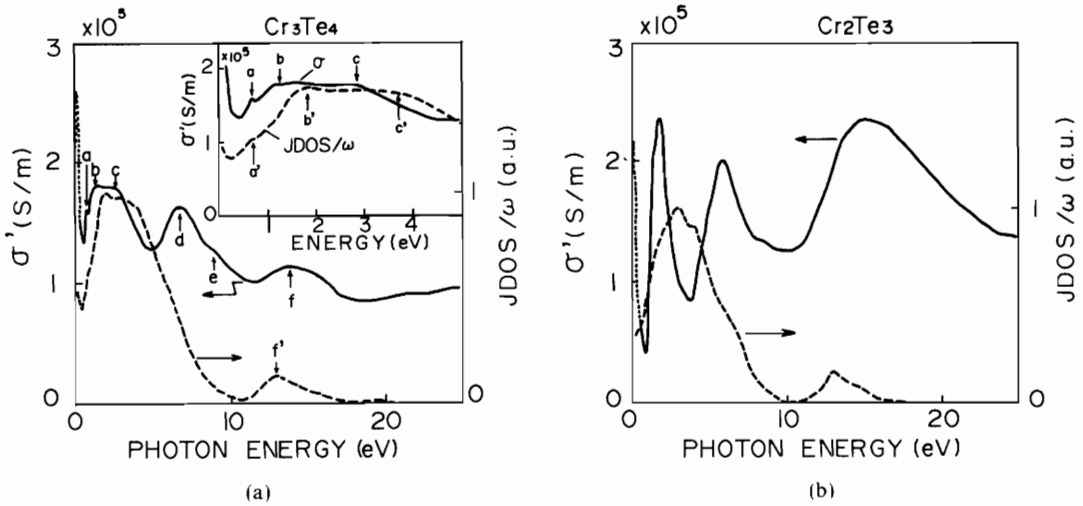

Fig. 4. Comparison between the experimental conductivity (real part) and the estimated JDOS (joint density of states) divided by photon energy for (a) Cr_3Te_4 and (b) Cr_2Te_3.

broad peak not very different from that in Cr_3Te_4. The discrepancy may result from the increased localized nature of Cr ions in Cr_2Te_3 due to the increase of the vacant cation sites in this structure. In such a case the simple convolution treatment for the optical conductivity becomes inapplicable and an appropriate treatment of the many-body effect should be considered.

For Cr_2Se_3 Dijkstra showed no DOS curves. He suggested that ferromagnetic Cr_2Se_3, if exists, would become "half-metallic", i.e. the energy gap would open up in the minority spin band, while it would not in the majority spin band. However, the existing material does not show ferromagnetism but is antiferromagnetic. The antiferromagnetism may result in the semiconducting properties of Cr_2Se_3. The observed spectrum seems to show an absorption edge around 0.3 eV. Infrared absorption studies in thin films will provide further information for the electronic structure of this material in the vicinity of the Fermi level. Calculation of the antiferromagnetic energy band structure of Cr_2Se_3 is necessary in order to discuss our optical results.

In conclusion, we measured optical reflectivity spectra in NiAs-type chromium chalcogenides between 0.3 and 23 eV at room temperature. Optical conductivity spectra were deduced from the reflectivity spectra. The conductivity spectrum of Cr_3Te_4 showed a reasonable agreement with the JDOS curve deduced from the reported energy band calculation. The low energy structures in the conductivity spectrum were interpreted in terms of band-to-band transition between chromium 3d and tellurium 5p states lying in the vicinity of the Fermi level. On the other hand, only a poor agreement between experiment and calculation was obtained in Cr_2Te_3. The necessity of a many-body treatment was suggested for the improvement of the correspondence. Band structure calculation on antiferromagnetic Cr_2Se_3 is desireable for the interpretation of the experimental spectrum of this crystal.

The authors express sincere thanks to Professor M. Yamaguchi of Yokohama National University for the kind suggestions for crystal growth. The authors are also grateful to Mr. T. Fukazawa of JASCO Ltd. for help in the ellipsometric measurements. We are also indebted to Dr. J. Dijkstra for informing us of their results of the band structure calculation on these crystals prior to publication.

References

1) S. Suga, K. Inoue, M. Taniguchi, S. Shin, M. Seki, K. Sato and T. Teranishi: J. Phys. Soc. Jpn. **52** (1983) 1848.
2) K. Sato: J. Phys. Soc. Jpn. **53** (1984) 1617.
3) M. Fujisawa, M. Taniguchi, S. Shin, H. Daimon, H. Sakamoto, K. Sato and S. Suga: *Proc. Int. Conf. Phys. Semicond., Stockholm* 1986, (World Scientific, Singapore, 1987) p. 1137.
4) K. Sato, H. Kida, M. Fujisawa and T. Kamimura: *Proc. Int. Conf. Magnetism, Paris* 1988, J. Phys. (France) **49** (1988) Suppl. C8, C8-37.
5) *Landolt-Börnstein*, New Series, **III/27a**, *Magnetic Properties of Pnictides and Chalcogenides*, ed. K. Adachi and S. Ogawa (Springer, Berlin, 1989) pp. 70–147.
6) K. Sato, Y. Aman and M. Hirai: *Proc. Int. Conf. Magnetism. Paris* 1988, J. Phys. (France) **49** (1988) Suppl. C8, C8-213.
7) Y. Aman, M. Hirai, M. Murayama and K. Sato: J. Magn. Soc. Jpn. **13** (1989) 183 [in Japanese].
8) J. Dijkstra: J. Phys.: Cond. Matt. **1** (1989) 9141.