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Optical properties and electronic structure of the misfit layer compounds 'LnNb₂X₅' (Ln ≡ Y, La or Nd; X ≡ S or Se)

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Abstract. We have determined the reflectance of the misfit layer compounds 'LnNb₂X₅' (Ln≡Y, Nd or La; X≡S or Se) between 50 meV and 6 eV for the electric field parallel to the layers. By fitting a Lorentz–Drude model the spectral distribution of the components of the energy loss function and of the conductivity function parallel to the layers were obtained. On the assumption of a charge transfer from the |LnX| to the |NbX₂| layers the values of the effective mass could be calculated from the intraband contribution to the optical spectra.

1. Introduction

The compounds 'LnNb₂X₅' (Ln≡Y, La or Nd; X≡S or Se) are built up of alternating layers of |LnX| and |NbX₂|, with |NbX₂| being a layered material which is formally intercalated by the |LnX| layer (figure 1). Two adjacent |NbX₂| layers are separated by a so-called van der Waals gap. The parameters b and c of the |LnX| and the |NbX₂| layers are similar in value whereas the parameters a have different values (irrational ratio), giving these compounds their name: 'misfit' layer compounds. The 'misfit' character of the two layers results in interesting electric and magnetic properties of these compounds [1].

The stability of the structure is based on electron transfer from the |LnX| layer to the |NbX₂| layer, giving rise to an Ln³⁺ ion which determines the magnetic properties of the material. The electrical conductivity is generally attributed to the |NbX₂| layer. As an example the superconductivity of the misfit compound depends on the presence of the |NbS₂| layer and its structural features (stacking mode: the 2H polytype is superconductive, and the 3R polytype is not) [2]. All materials investigated here are metals with 'LaNb₂Se₅' being a superconductor at 5.5 K [3].

There have been investigations of the electronic structure of misfit layer compounds, notably by Ohno [4] who determined the drop in energy of the Sm 4f band of the |SmS| part of 'SmNbS₃' compared with Sm 4f band of the SmS binary.

This is one of the first optical studies of this class of materials (see also [10] for a study of 'CeNb₂S₅'). Nevertheless there are several optical studies of monochalcogenides and also of NbSe₂ which can be used for comparison [5,6].
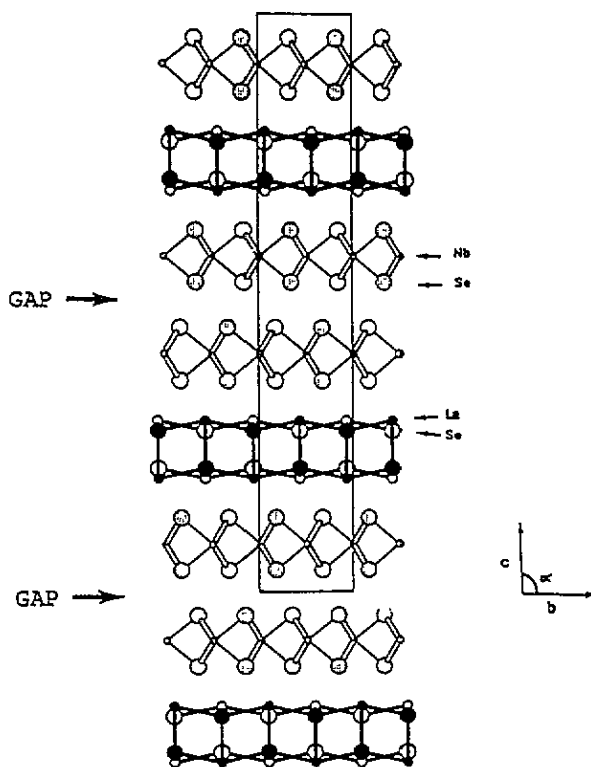
Figure 1. Projection of the complete structure of 'LaNbSe$_5$' along the misfit axis ($\alpha = 90°$).

2. Experimental procedure

The elements La, Nb and X were sealed in an evaluated silica tube in 1:2:5 stoichiometry. The tube was then heated to 1050 °C, kept there for 15 d and afterwards slowly cooled to room temperature. A final crystal growth procedure was not necessary because crystals were already present in the tube. The single crystals are platelets which can easily be split.

The crystals showed highly reflecting shiny (001) surfaces with lateral dimensions between 1 mm × 2 mm and 3 mm × 3 mm. To improve the flatness of the investigated surfaces the layered crystals were cleaved using adhesive tape. The reflection measurements were performed at near-normal incidence with the electric field parallel to the (001) plane, in the range of photon energies between 50 meV and 6 eV, using a single-beam spectrometer designed for the investigation of small samples. Therefore, the absolute values of the reflectance data could be improved further by restricting the area investigated to a spot size of 0.5 mm × 0.2 mm. All spectra were taken at room temperature.

3. Results and discussion

The reflectance spectra of 'LaNb$_2$S$_5$', 'LaNb$_2$Se$_5$', 'NdNb$_2$S$_5$' and 'YNb$_2$S$_5$' are shown in figure 2. They are characterized by very pronounced plasma edges with spectral positions between 0.6 and 0.7 eV and high values of about 90% for the reflectivity at low energies,
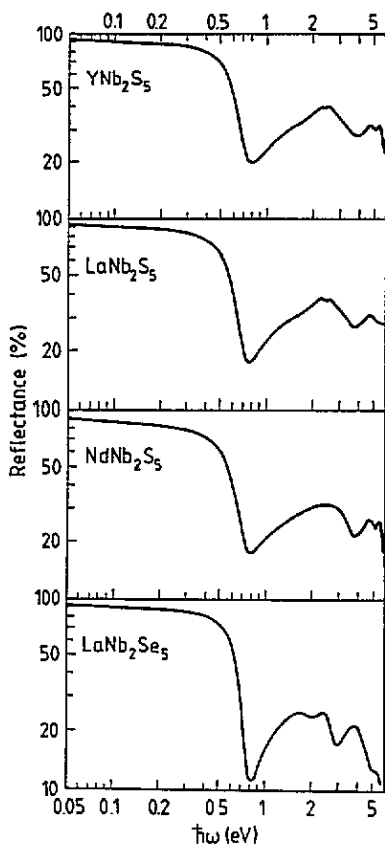
Figure 2. Reflectance spectra of (001) surfaces of YNb₂S₅, LaNb₂S₅, NdNb₂S₅ and LaNb₂Se₅ single crystals ($T = 300$ K).

typical features of metallic behaviour. At higher energies the reflectivity decreases to minimum values between 10 and 20%, followed by broad maxima associated with electronic interband transitions in the |LnX| and |NbX₂| layers [5].

For a quantitative analysis of the optical data we have determined the spectral distribution of the real and the imaginary parts of the dielectric functions by fitting a Lorentz–Drude model to the reflectance spectra. The results were used to calculate the in-plane tensor components of the energy loss functions $\text{Im}(-1/\epsilon) = \epsilon_2^2/(\epsilon_1^2 + \epsilon_2^2)$ and of the conductivity functions $\sigma = \epsilon_0\omega\epsilon_2$, plotted in figures 3 and 4, respectively. The loss functions reflect the longitudinal modes of these compounds which can be excited by electron beams. The most prominent longitudinal mode of each material is the plasmon peak of the free carriers at the screened plasma energy of around 0.65 eV. The conductivity functions are related to the transverse modes excited by electromagnetic radiation. Above a photon energy of 1 eV these excitations are *interband* transitions which are described in our model by a number of Lorentz oscillators. In the low-energy region the main contribution is due to *intraband* transitions, represented in our model by a single Drude term. In this model the square of the unscreened plasma frequency ω_p represents the oscillator strength; the scattering rate $1/\tau$ is the half-width of these excitations, $\sigma_0 = \epsilon_0\omega_p^2\tau$ being the optical value of DC conductivity. The parameter values resulting for the different compounds are
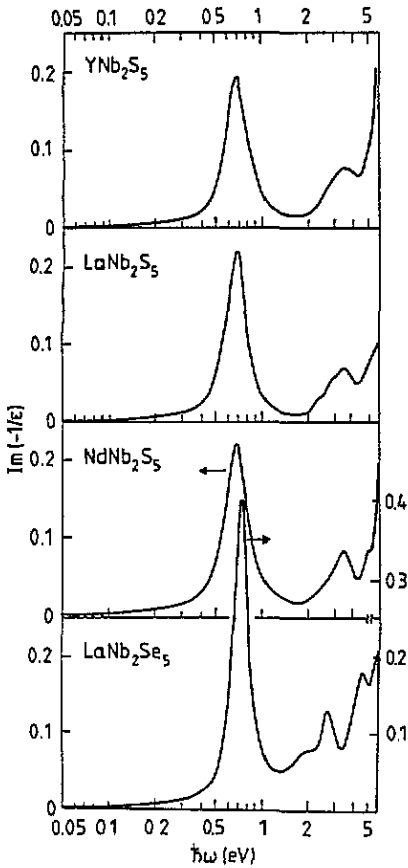
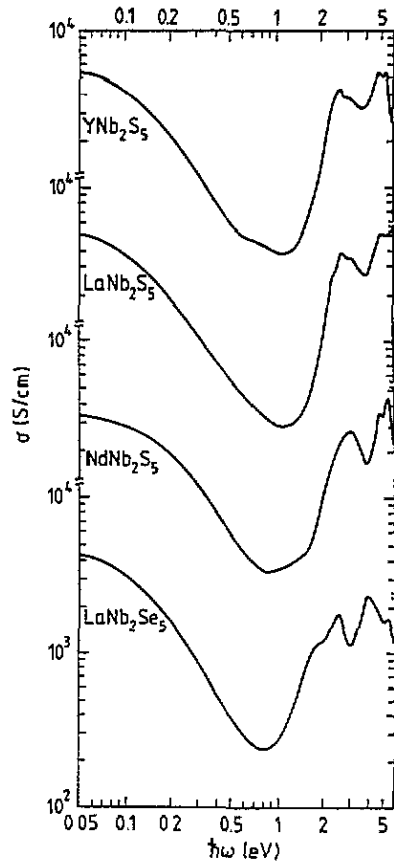Figure 3. Energy loss functions, obtained by a Lorentz–Drude fit from the reflectance spectra in figure 2.

Figure 4. Conductivity functions, obtained by a Lorentz–Drude fit from the reflectance spectra in figure 2.

Table 1. Electronic transport parameters of YNb_2S_5, $LaNb_2S_5$, $NdNb_2S_5$ and $LaNb_2Se_5$ at 300 K.

	ω_p (s^{-1})	$1/\tau$ (s^{-1})	σ_0 ($s\ cm^{-1}$)	N (formula units)	N ($10^{21}\ cm^{-3}$)	Hole mass (units of m_0)
YNb_2S_5	3.95×10^{15}	2.3×10^{14}	6.0×10^3	0.72	4.20	1.78
$LaNb_2S_5$	3.64×10^{15}	2.0×10^{14}	5.9×10^3	0.86	4.77	1.33
$NbNb_2S_5$	3.60×10^{15}	3.3×10^{14}	3.5×10^3	0.82	4.60	1.35
$LaNb_2Se_5$	3.42×10^{15}	2.1×10^{14}	4.9×10^3	0.86	4.56	1.23

compiled in table 1.

For a calculation of the effective mass m^* according to the relation

$$\omega_p^2 = Ne^2/\epsilon_0 m^*$$

we estimate the value of the free-carrier concentration by discussing the charge transfer in these compounds. There is a charge transfer from the |LnX| layers (Ln $\equiv$ Y, La or Nd;

X ≡ S or Se) to the |NbX$_2$| layers, resulting in the valency states Ln^{3+}X^{2-}. However, this is only the case if there are two |NbX$_2$| layers present. In 'LaNbS$_3$' (only one NbX$_2$ layer) the charge transfer from the |LnS| to the |NbS$_2$| layer amounts to only 0.86 e$^-$ per La [7]. In 'LaNb$_2$S$_5$' (and in the other products incorporating two |NbX$_2$| layers), magnetic measurements confirm that there is a transfer of one complete e$^-$ from |LaS| to |NbS$_2$|, resulting in a net magnetic moment of zero in |LaS| [8]. Within the |NbX$_2$| layers, four of the five valence electrons of each Nb atom are transferred to the respective two chalcogen atoms, constituting the X^{2-} anions. Therefore, there are three electrons per formula unit which occupy the lowest d bands of two Nb ions. This means that these two d bands are three quarter filled which corresponds to two one quarter bands of p-type conduction, i.e. to a free-carrier concentration, of one hole per formula unit. Using the exact stoichiometric and unit-cell data for 'LaNb$_2$Se$_5$' ($\equiv$(LaSe)$_{1.14}$(NbSe$_2$)$_2$) results in a carrier concentration of 0.86 holes per formula unit, i.e. $N = 4.56 \times 10^{21}$ cm^3 and a hole mass of 1.23m_0. The other compounds have similar values (see table 1). If the optically determined conductivity values are compared with the DC conductivity values, the values are in about the same range. It has to be considered that the electrical conductivity can only be determined down to a certain degree as the sample thickness cannot be determined exactly.

As mentioned above, the steep increase in the conductivity function above 1 eV, observed in the misfit compounds investigated, is due to direct transitions between the valence bands and the lowest unoccupied states of the conduction bands. In both types of layer the valence bands are composed of chalcogen p orbitals whereas the conduction bands are derived from d orbitals of the metal ions. A comparison of the optical absorption of the misfit compounds with the spectra obtained on the LnX and NbX$_2$ parent compounds [6, 9] allows the following qualitative conclusions to be drawn. The lower interband excitations are mainly correlated to the niobium chalcogenide layers and the higher excitations to the lanthanide monochalcogenide layers, indicating a higher band gap in the |LnX| layers. On the other hand, the gap energy in the |NbX$_2$| layers is further lowered, replacing the sulphur by selenium ions. A quantitative split of the dielectric function of 'LaNb$_2$Se$_5$' e.g. into the separate contributions of both types of layer, cannot easily be performed because the values of the free-carrier concentration in the parent compounds are completely different from the situation in the misfit compounds. Therefore, it requires a careful analysis of the free-carrier effects in the parent compounds, including the Burstein shift. This will be done in a separate paper.

4. Conclusion

Electronic transport properties of 'misfit' layer compounds have been, up to now, rarely investigated by optical methods. The results can help to understand those compounds and combined with band-structure calculations might answer the stability question. It would be interesting to combine the results obtained with band-structure calculations.

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