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Effect of exchange splitting on the low-energy optical absorption in heavy rare-earth metals

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Abstract. A detailed experimental investigation of the temperature dependence of the resonance anomaly on the dispersion curves of optical conductivity has been carried out on single crystals of Gd, Tb and Dy. This dependence is related to electron transitions between valence states split by the exchange field of the 4f shell. Over the entire temperature range of existence of the optical conductivity peak, its position on the energy scale is stable. Magnetic phase transitions of the ferromagnet–spiral type have not brought about any noticeable changes of peak parameters. The theoretical interpretation of the properties of the observed anomaly is based on direct calculations of the electronic structure and interband density of states for ferromagnetic and spiral configurations of magnetic moments. It is shown that, in the electronic spectrum of rare-earth metals, there is a region that remains relatively stable in the course of changes of the magnetic configuration and is responsible for the stability of the energy localization of the investigated peak.

1. Introduction

The possibility of detecting anomalies in the frequency dependence of the optical characteristics of rare-earth metals (REM) at energies close to the value of the valence states split by the exchange field of the 4f electrons was predicted by Miwa (1963). It was assumed that the parameters of these features would depend essentially on the type of magnetic structure.

A number of experiments conducted initially on polycrystalline REM, and then on single crystals, have confirmed the presence of 'magnetic' peaks (MP) on the dispersion curves of optical conductivity of heavy REM. The positions of these peaks were proportional to the spin moment of the isolated atom shell (Krizek and Taylor 1975, Weaver and Lynch 1975, Knyazev and Noskov 1977). It was also noted that the intensity and localization of the peak on the energy scale do not suffer any stepwise changes during transition from the spiral configuration of atomic moments to a collinear one, as a result of both a temperature change and application of a magnetic field.

A detailed experimental investigation of the temperature dependence of MP in gadolinium is reported by Beznosov *et al* (1984a, b) and Knyazev and Bolotin (1984). At all temperatures below the Curie point T_C a distinct peak could be observed in the

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optical conductivity. The height of the peak decreased rapidly on heating, while the position remained unaltered. No MP was observed in REM in the paramagnetic region.

The stability of energy gaps between electron levels despite changes of magnetic characteristics, expressed as a constant position of MP, is not a trivial experimental result. This is in contrast to the commonly acknowledged strong dependence of the electronic spectrum and many physical properties on the magnetic structure (Taylor and Darby 1974). It should also be noted that the mechanism of disappearance of the MP observed in the experiment (i.e. gradual diminution of intensity, constant position being preserved) contradicts in principle Stoner's theory of average field in a ferromagnet, which assumes that the exchange splitting of valence states is proportional to the macroscopic magnetization. In the latter case the vanishing of the peak on heating would take place by way of its displacement to zero electron transition energy.

The number of theoretical investigations in which MP properties are discussed are very few. Watson *et al* (1968) considered the change in the electronic structure of the non-magnetic state of REM in the course of magnetic ordering, using the single-band model and perturbation theory. Estimates have shown that for some regions of reciprocal space the transition from ferromagnetic structure to spiral structure leads to changes of the electronic spectrum that are of the same order as the value of exchange splitting of ferromagnetic states. However, this calculation does not allow one to consider the problem to be solved, not only on account of the accepted approximations, but also because of the fact that in a ferromagnet the exchange gap divides pairs of states of opposite spins over the entire Brillouin zone, whereas in the case of spiral structure corresponding changes have been obtained only for a limited reciprocal-space region. Hence with such an approach the transition from spiral structure to a ferromagnetic one must lead to a fundamental change in the parameters of the observed peak, but this does not correspond to the experiment.

In the papers of Beznosov *et al* (1984a, b) devoted to the study of the thermal properties of MP in gadolinium, a simple theoretical model was used, which assumed that the hopping integral (or, what is equivalent, the energy bandwidth) for electrons responsible for the peak is much smaller than the splitting due to exchange interaction with 4f electrons. Such a relationship between parameters stipulates a strong bonding between an electron and 4f shells, implying that the valence electron moving about the crystal aligns its spin with the atomic spins. As a result, the energy of electron transitions responsible for the MP is determined by the Zeeman splitting of valence states by the internal exchange field of the 4f shell and depends little on the mutual orientation of atomic magnetic moments. Hence, the dependence of electron states on the magnetic moment configuration was not considered. It should be noted that the assumption of small energy band widths used in these investigations, and, consequently, the inference of their weak dependence on the configuration of atomic magnetic moments, does not agree with the results of band calculations of ferromagnetic and non-magnetic phases of REM (Harmon 1979, Temmerman and Sterne 1990).

A preliminary discussion of the special features of MP based on the first direct calculations of the electronic structure and interband density of states of the non-collinear configuration of heavy REM are given by Sandratskii (1989).

In this report a detailed experimental investigation of the temperature dependence of MP on dispersion curves of optical conductivity of single crystals of Gd, Tb and Dy has been carried out. The discussion of the results obtained is conducted within the framework of the approach proposed in the work of Sandratskii (1989).

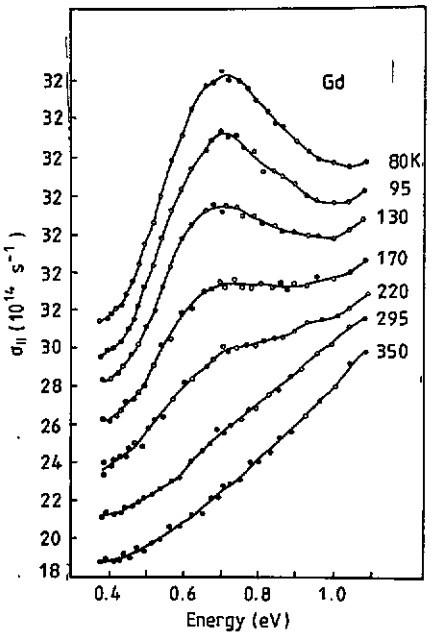

Figure 1. Dispersion of optical conductivity ($E \| c$) of Gd single crystal at different temperatures. Each curve is displaced by 2×10^{-14} s^{-1}.

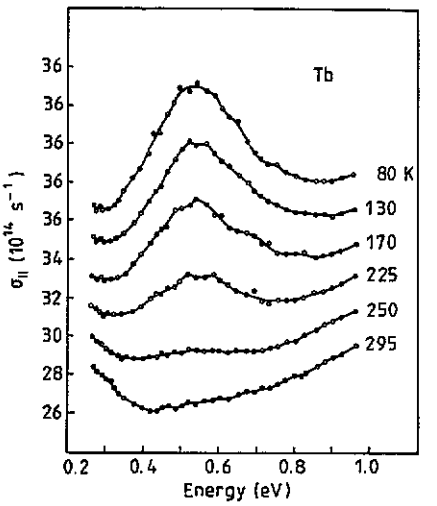

Figure 2. Same as in figure 1 for Tb.

2. Experiment

The measurements of spectral characteristics were conducted by the ellipsometric method in an optical cryostat in the temperature range 80–295 K (Tb, Dy) and 80–350 K (Gd) in a vacuum of 10^{-6} Torr. Specimens with a reflecting surface containing a hexagonal c axis were polished by an electrolytic method proposed in Weaver and Olson (1977). The tensor components of the refractive and absorption indices of the single crystals were measured in the region of formation of MP, which corresponds to two mutually perpendicular orientations of the electric vector E of the light wave and the c axis ($E \| c$ and $E \perp c$). The calculation of spectral characteristics was based on formulae taking into account corrections for the optical uniaxiality of the crystal (Knyazev and Maevskii 1984). Experiments revealed the existence of MP in both components of optical conductivity $\sigma_{\parallel}$ and $\sigma_{\perp}$, but because of high anisotropy of absorption its intensity in the longitudinal component was much higher. In order to determine the interband optical conductivity, the intraband contribution obtained from measurements in the infrared range of the spectrum, where the effect of quantum absorption diminishes sharply, was subtracted from the experimental dispersion curve σ.

The longitudinal component of the optical conductivity $\sigma_{\parallel}$ of single crystals of Gd, Tb and Dy in the region of emergence of MP is shown in figures 1–3 at various temperatures. The MP maximum localization energies diminish with increasing REM atomic number and are equal to 0.70 eV (Gd), 0.54 eV (Tb) and 0.49 eV (Dy). In the investigated temperature range Gd ($T_C \sim 293$ K) passes from the ferromagnetic to the paramagnetic state, while Tb ($T_C \sim 221$ K, $T_N \sim 229$ K) and Dy ($T_C \sim 85$ K, $T_N \sim 178$ K) pass consecutively through three phases, ferro-, antiferro- and paramagnetic.

The analysis of figures 1–3 show that the following are the most prominent features of MP. (i) The MP position on the energy scale is higher the greater the magnitude of the magnetic moment of an isolated atom. (ii) Changes in the magnetic structure do not bring about any considerable change in the shape or position of MP. (iii) No peak is observed in the high-temperature region. Besides, the experiment showed that for all three metals the peak disappears by way of gradual 'washing out' with increasing temperature, the MP energy position being preserved throughout its temperature range of existence.

3. Calculations

Neglecting relativistic effects, we can express the one-electron Hamiltonian of a non-collinear magnet as follows (Sandratskii and Guletskii 1986, Sandratskii 1986):

$$H = -\Delta + \sum_j U^j V(|r - a_j|)(U^j)^{-1} \tag{1}$$

where a_j is a radius vector of the jth atom; the matrix of spin rotations U^j determines the transition between the laboratory system of coordinates and the local atomic systems of coordinates, the z axis of which is parallel to the direction of the moment of the relevant atom. The potential V in (1) is

$$V(r) = \begin{pmatrix} V_+(r) & 0 \\ 0 & V_-(r) \end{pmatrix}. \tag{2}$$

The subscripts 'plus' and 'minus' refer to spin indices relative to the local quantization axis.

In this investigation the calculations were made for simple spiral structures

$$e_j = (\cos(q \cdot a_j), \sin(q \cdot a_j), 0) \tag{3}$$

where e_j indicates the direction of the jth atomic moment and q is the spiral vector. In the case of spiral magnetic structures it is possible to show that for arbitrary spiral parameters the electronic spectrum consists of energy bands continuous in the HCP lattice Brillouin zone.

The Korringa–Kohn–Rostoker (KKR) method was used to calculate the electronic spectrum in the case of non-collinear magnetic structures (Sandratskii 1986). The spin-polarized potential of Tb (Matveeva and Egorov 1981) was employed to calculate the phases of single-centre scattering corresponding to orbital quantum numbers $l = 0, 1, 2$. It was assumed that the main change of valence electron states in the course of transition from one heavy REM to another is associated with the difference in the number of 4f electrons and, consequently, with the magnitude of the local exchange field of the 4f shell. This makes it possible to simulate the transition from one REM to another by changing the spin polarization of valence electron potentials inside the atomic spheres

$$V_\beta(r) = \tfrac{1}{2}[V^0_+(r) + V^0_-(r)] + \alpha\beta\tfrac{1}{2}[V^0_+(r) - V^0_-(r)] \tag{4}$$

where $\beta = \pm 1$ is the spin index relative to the local atomic quantization axis, V^0_β is the

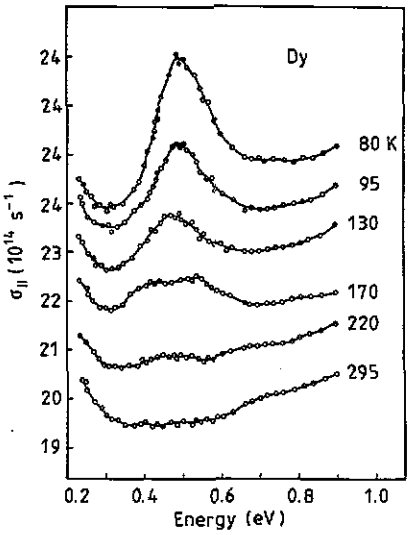

Figure 3. Same as in figure 1 for Dy. Each curve is displaced by 10^{-14} s^{-1}.

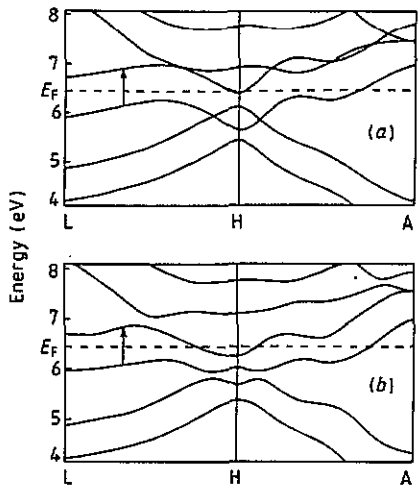

Figure 4. The section of the electronic energy spectrum for $\alpha = 1$: (*a*) ferromagnetic configuration; (*b*) spiral configuration corresponding to $\theta = 45°$. The arrows mark the transitions between congruent energy levels.

potential of Matveeva and Egorov (1981) and α is a constant varying the magnitude of spin polarization.

The optical parameters of the crystal at a certain frequency of the light wave are characterized by the number of electron states permitting a quantum transition at this frequency, as well as by the probability of these transitions. In this paper we consider the first factor only determined by the magnitude of the interband density of states (IDOS):

$$N_j(E) = (1/\Omega) \sum_{s,f} \int \delta[\varepsilon_f(k) - \varepsilon_s(k) - E] \, dk \tag{5}$$

where ε_f are the occupied states and ε_s are empty states; the integration is carried out over the Brillouin zone and Ω is the volume of the Brillouin zone.

4. Results of calculation and discussion

The general characteristics of electronic spectra of ferromagnetic and non-magnetic configurations of atomic moments can be seen in figure 4. Figure 4(*a*) shows part of the spectrum of a ferromagnet wherein the position of bands relative to the Fermi level allows transitions between states of spin sub-bands split by the exchange field of the 4f electrons. Figure 4(*b*) shows the relevant part of the spectrum of a spiral structure. The spiral structure features an angle of 45° between atomic magnetic moments of neighbouring ferromagnetic layers, this being close to the maximum value of 50° (Taylor and Darby 1974) observed for REM. Note that experiments show the tendency of this angle to increase with heating.

In the case of a ferromagnet (figure 4(*a*)) the energy spectrum breaks up into band pairs, which correspond to opposite spin projections and are practically congruent to one another throughout the entire Brillouin zone. Because of this, the electron transitions between spin sub-bands occur at practically constant energy, determined by the exchange interaction between electron states and 4f-shell spins. This leads to considerable intensity of absorption at the exchange splitting frequency despite the relatively small probability of transitions between states of opposite spins. (The main contribution to the probability of transitions is associated with spin–orbit interaction effects not considered here.)

In the case of non-collinear structures, electronic states are no longer characterized by a certain spin projection onto some quantization axis, but have non-zero spinor values corresponding to both spin projections. The character of changes of bands forming MP during a transition from ferromagnetic (figure 4(*a*)) to spiral (figure 4(*b*)) configuration of atomic moments depends substantially on the point in reciprocal space. Near point L the bands are still almost congruent, although the congruence condition is fulfilled somewhat worse than in the case of a ferromagnet. Near points A and H one observes intersections between various band pairs. If transition is made to a non-collinear structure, the intersecting energy bands interact intensively (Sandratskii and Guletskii 1986, 1989), leading to elimination of degeneracy and substantial restructuring of the spectrum in this region.

Calculations have shown that near point L, where a high degree of congruence is preserved, the maximum admixture of states with opposite spin projection on local axes is close to 15%. On the other hand, near points A and H, where hybridization interaction of bands takes place, the admixture of states of opposite spin attains 30–35%. Since strong hybridization changes occur predominantly in those regions of the spectrum where both bands lie above the Fermi level, the main contribution to optical absorption depends on the almost congruent regions. However, a considerable number of electron transitions occur also between parts of the spectrum changed by hybridization interaction (see, for example, direction AH). This must disturb the resonance character of transitions for this part of the states and make the anomalies of optical characteristics less marked. These conclusions, in our opinion, are confirmed by the character of the optical conductivity temperature dependence (figures 1–3). The gradual drop in intensity observed experimentally and the smearing of MP with increasing temperature without any substantial change in localization on the energy scale testified to non-stepwise change in the character of considered parts of the band spectrum during transitions to a non-ordered state of magnetic moments.

Calculation of the electronic spectrum for the same two magnetic structures, but with a lower 4f-electron exchange field value corresponding to $\alpha = 0.613$, has shown that in the case of transition to a spiral, a considerably more important disturbance of band congruence occurs than for $\alpha = 1$. The decrease of exchange field also affects the partial spin composition of states. Thus for the parts of bands isolated by energy the admixture of states with opposite spin projection on local axes attains one-third, while for the hybridized part it is 43%.

The properties of electron band structure mentioned above have an effect on the shape of IDOS curves shown in figure 5 for two values of parameter α and various values of vector $\boldsymbol{q}$. In the case of a ferromagnetic configuration ($\boldsymbol{q} = 0$) the transitions between states of congruent bands split by the exchange field determine the presence of sharp spikes of IDOS at energies close to 0.8 eV and 0.5–0.6 eV for values of α equal to 1 and 0.613, respectively. The 0.8 eV value corresponds to the peak position experimentally observed for Gd, while the 0.5–0.6 eV energy corresponds to that of Tb and Dy.

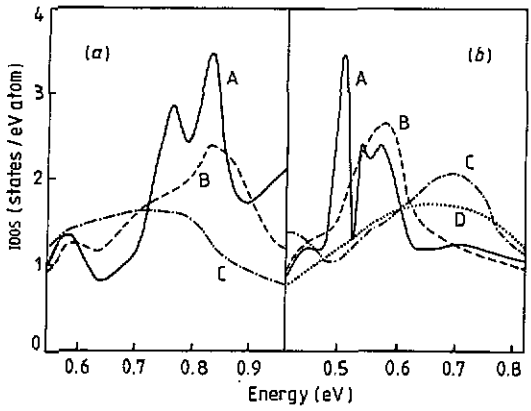

Figure 5. Joint density of states: (*a*) $\alpha = 1$, $\theta = 0°$ (curve A), 45° (curve B), 90° (curve C); (*b*) $\alpha = 0.613$, $\theta = 0°$ (curve A), 22.5° (curve B), 45° (curve C), 90° (curve D).

The analysis of figure 5 shows that for each value of the local exchange field there is an interval of vectors q, or, what is equivalent, of angles θ between the spins of neighbouring ferromagnetic layers, for which the MP position does not suffer any noticeable change. With further growth of θ the shape of the curve changes considerably. The stability of MP position depends directly on the presence of a region of the electronic spectrum for which band congruence and the spacing between bands are to a considerable extent preserved for a definite interval of angles θ. Further growth of θ leads to the break-up of congruent bands in this part of the spectrum and to a considerable change of IDOS curves in the neighbourhood of MP.

It follows from the calculation results that band congruence and the spacing between bands for a part of the spectrum near point L are preserved until, in this part of the spectrum, the effect of the intra-atomic exchange field of the 4f shell, bringing about the Zeeman splitting of valence states, predominates over the tendency, which increases with increase of inter-spin angle θ, to hybridization of electron states with opposite spin projections on local atomic axes. Thus, the use of a physical model proposed by Beznosov *et al* (1984a, b), and assuming weak spin hybridization of valence states, is justified for the qualitative description of optical properties associated with MP.

It should be noted that, although we studied the effect of atomic moments for spiral structures, other investigations (Sandratskii and Guletskii 1989) make it possible to assume that the obtained conclusions on the character of changes in the spectrum can be extended to arbitrary magnetic configurations with close values of the mean angle between atomic spins, i.e. can be used not only for the analysis of a transition from the ferromagnetic structure to a spiral one, but also for the process of spin disordering. Note also that as the appearance of MP is connected with the constancy of interband distance at various points of the Brillouin zone, this property is not reflected by the density of states (DOS), because DOS contains information only about energy (not spatial) position of individual electron states. The transition from ferromagnetic to spiral structure leads to rather weak changes of the DOS, which have no importance for the question discussed. Therefore we do not represent the DOS curves.

5. Conclusions

The detailed experimental investigations of the temperature dependence of MP in optical conductivity curves of Gd, Tb and Dy have shown the high stability of the peak position over the entire temperature range of its existence. Calculations of the electronic spectrum for ferromagnetic and non-collinear magnetic structures have allowed us to reveal a region in k-space that has not undergone any substantial changes over a considerable range of angles between spins of neighbouring atoms. Substantial changes occurring in another part of the spectrum, brought about by the non-collinearity of atomic moments, must have an influence on the topology of the Fermi surface. These changes have to be taken into account when one considers the energetic advantages of one or other magnetic configuration.

The experiment confirms the non-stepwise evolution of MP with change of temperature predicted by calculations. Calculation results make it possible to relate the observed decrease of peak height with rise of temperature to the gradual breakdown of congruence of energy bands resulting from the growth of angles between neighbouring spins. Such an explanation disagrees with Stoner's theory of average field, in accordance with which the disappearance of MP should take place through its displacement into the region of low energies.

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