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Magnetic excitations in intermediate-valence semiconductors with a singlet ground state

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Abstract. An explanation of the origin of inelastic peaks in magnetic neutron-scattering spectra of the mixed-valence semiconductor SmB_6 is proposed. It is shown that the excitonic theory of the intermediate valence state not only gives the value of the peak frequency but also explains the unusual angular dependence of the intensity of inelastic magnetic scattering and describes the dispersion of magnetic excitations in good agreement with experiment.

1. Introduction

Although the intermediate-valence (IV) rare-earth semiconductors have been studied both experimentally and theoretically since the 1960s, the microscopic description of their ground state and the nature of valence fluctuations is still a matter of discussion. A new splash of interest in IV systems with anomalously narrow energy gaps is connected with the appearance of several new Ce-based and U-based Kondo lattices with semiconductor-like behaviour at low temperatures (see, e.g., [1]). Several mechanisms of gap formation in IV systems have been proposed during the last two decades. Among these mechanisms the on-site fd-hybridization gap [2, 3] and weak Wigner crystallization of the f electrons in the low-carrier limit [4] should be mentioned. Recently a model of the 'Kondo insulator' with filled heavy-fermion bands in a ground state was proposed [5]. On the other hand the idea of the excitonic insulating state can be traced through the whole history of the IV systems (see [6, 7, 8] and references therein).

Among the systems with low carrier density and microgaps in the electron spectra, the non-magnetic IV semiconductors SmS and SmB_6 are the most thoroughly studied compounds, and the whole scope of the experimental data gives a firm base for choosing among different theoretical models. Previous studies of anomalous vibration spectra in optical- and neutron-scattering experiments [9, 10, 11] gave strong arguments in favour of the model of an excitonic insulator for SmB_6 and SmS with characteristic soft charge-transfer valence fluctuations and spin excitations specific for the IV phase. Recently an inelastic peak in the magnetic neutron-scattering spectra of SmB_6 with energy $\approx$14 meV was discovered [12]. Later on the strong anisotropy and temperature dependence of magnetic scattering was discovered [13] and very recently it was shown that the magnetic excitations are coherent and have a noticeable dispersion [14]. In response to this challenge we present here the theoretical explanation of all these features within the excitonic-insulator model of the IV semiconductors.

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2. Theory of magnetic scattering in the intermediate-valence semiconductors

Samarium sulphide and hexaboride have a singlet ground state which means that the Sm ions in an IV state have the same value of the total angular moment $J = 0$ as the Sm^{2+} ion in the divalent state. According to the general picture of excitonic-type valence fluctuations in the IV semiconductors [7, 11] the electronic configuration of Sm ions in the IV phase is changed from the divalent $f^6(^7F_0)$ state to a mixed state $\tilde{f}^6(^7F_0) = f_{J=5/2}{}^5f^*_{j=5/2}$. The many-particle interaction results in forming a double-well potential for the last f^* electron. The inner valley of this potential is formed by purely intra-atomic forces within the central Sm ion, and the outer valley enveloping the neighbouring atoms arises due to the attractive Coulomb interaction between the electron trying to leave the f shell because of the fd and fp hybridization and the hole left in this shell. Hence, the f^* electron is poised between two valleys in the ground state and can be excited to the higher states of the double-valley potential (or leave it for the conduction band). These excitations are the valence fluctuations which are seen in the thermodynamic and resonance properties of the IV semiconductor.

The singlet ground state of this system can be represented by the trial wave function

$$|\Psi_g) = \prod_m^A \psi_{m,g} \tag{1}$$

describing the IV state as the antisymmetrized product of the single-site 'bonding' linear combinations

$$\psi_{m,g} = \cos\theta|f^6_m, {}^7F_0) + \sin\theta|f^5_m B^{(f)}_m, {}^7F_0) \tag{2}$$

(see [7]). Here θ is the parameter characterizing the degree of valence mixing, and B_m defined as

$$B^{(f)}_m = \sum_j F(j) b^+_{c,m+j} b_{f,m}|f^6_m, {}^7F_0) \tag{3}$$

describes the combination of the electron–hole pairs with appropriate symmetry allowing us to construct the singlet $^7F_0$ state centred at site m of the 'core' f^5_m and the 'loosely bound' electron shared between the central site and its nearest environment. Here b_f (b^+_c) is the annihilation (creation) operator of the electron in the f shell (conduction band); $F(j)$ is the envelope function extended at least up to the nearest neighbours in the cationic sublattice.

In the integer valence case ($\theta = 0$) the lowest local charge excitations in this sublattice are the on-site fluctuations $f^6_m \rightarrow f^5_m d_m$ with the energy $\hbar\omega \approx 0.8$ eV, and the lowest spin excitations are the intermultiplet transitions $f^6_m(^7F_0) \rightarrow f^6_m(^7F_1)$ having the energy $\hbar\omega = 0.036$ eV . In the IV case ($\pi/2 > \theta > 0$) characteristic charge-transfer excitations to the antibonding states

$$\psi_{m,ex} = -\sin\theta|f^6_m, {}^7F_0) + \cos\theta|f^5_m B_m, {}^7F_0) \tag{4}$$

and spin excitations with a moment reversal

$$\psi_{m,ex} = \cos\theta|f^6_m, {}^7F_1) + \sin\theta|f^5_m B_m, {}^7F_1) \tag{5}$$

are possible.

The first of these excitations describes the charge valence fluctuations. These excitations were found to be responsible for the strong anomalies in the phonon spectra of SmS and SmB_6 in the IV state. The 'fingerprint' of this branch is the spatially extended component $B^{(f)}_m$ (3). Its Fourier transform determines the characteristic q dependence of phonon softening in these systems [10, 11]. Here we show that the second excitation involving the spin of Sm ions is the source of magnetic scattering in a singlet IV semiconductor,

and again the decisive argument will be the contribution of the extended part (3) of the wave function (5) to the magnetic form factor which determines both its Q dependence and anisotropy.

Let us, first, estimate the energy of the excitation $^7F_0 \rightarrow {}^7F_1$ from the ground state (2) to the excited state (5). The energy of conventional transition $E[f^6(^7F_0) \rightarrow f^6(^7F_1)] \approx 36$ meV is defined by the matrix element of the operator of spin–orbit interaction $\xi(r) = -[(1/2c^2)r]\,\partial V(r)/\partial r$.

$$\Delta_{so} = (f^6|\xi(r)|f^6). \tag{6}$$

The IV state of Sm can be treated in spectroscopic terms as a mixed configuration $\tilde{f}^6 = f^5f^*$ described by equation (2). One adopts for such a configuration the LS coupling scheme for the moments of the localized electrons in a 'core' f^5 and the jj scheme for coupling with the last f^* electron. Hence the fine structure of the excitation spectrum is determined by the matrix element $\Delta^*_{so} = (f^*|\xi(r)|f^*)$ instead of (6). Then taking into account the extreme localization of the spin–orbit operator $\xi(r)$ one can estimate the energy of spin–orbit splitting in the IV state as $\Delta^*_{so} = \cos^2\theta\,\Delta_{so} \approx 16$ meV if the value of 2.55 is assumed for the Sm valence in SmB_6. This value is in reasonable agreement with the experimental energy of the inelastic peak in the neutron-scattering spectrum [13].

This peak demonstrates strong dependence on both the value and orientation of the momentum transfer vector Q. The Q dependence of the intensity of inelastic magnetic scattering on a singlet MV semiconductor is determined by the magnetic form factor $I(Q) \sim |G(Q)|^2$ which has the form

$$G(Q) = (\psi_i|e^{iQ\cdot r}|\psi_f). \tag{7}$$

Here $\psi_{i,f}(r)$ are the spatial components of initial- and final-state wave functions (equations (2) and (5), respectively). When studying the form factor connected with magnetic excitation of the loosely bound f^* electron we can assume $\psi_i \approx \psi_f$ for the orbital part of the wave function.

To calculate $G(Q)$ we use in B_m (3) the LCAO of Γ_{2u} symmetry consisting of boron p and samarium d orbitals centred on the lattice sites of two nearest coordination spheres. For example the only LCAO of Γ_{2u} symmetry which can be constructed of the nearest-neighbour atomic d orbitals of the Sm sublattice is

$$B(r) = \frac{1}{\sqrt{6}}[d_{yz}(100) - d_{yz}(\bar{1}00) + d_{xz}(010) - d_{xz}(0\bar{1}0) + d_{xy}(001) - d_{xy}(00\bar{1})]. \tag{8}$$

It is easily seen that the maxima of the electron density for such an angular distribution fall on the spatial diagonals [111] and form bonding states with the f_{xyz} harmonic. A similar combination can be constructed for the boron p orbitals. To model the spatial distribution of the electron density we approximate these orbitals by Coulomb radial functions. The results of the calculations of form factor $I(Q)$ together with the experimental data are presented in figure 1, and the spatial density distribution which determines the angular anisotropy of the form factor is shown in figure 2. It is seen that even such a rough model gives a good qualitative description of this anisotropy. Our fitting demonstrates also the dominant contribution of boron p orbitals in the wave function B_m (3): the maximum of the charge distribution is close to the facet of the boron cluster.

Recent neutron-scattering studies [14] also revealed a noticeable dispersion of the 14 meV excitation. This dispersion was registered both in [111] and [011] directions of the Brillouin zone. Such a dispersion can be considered as strong indication of a coherent character of magnetic excitations in IV semiconductors. To check this assumption we calculated the dispersion law $E(q)$ for the exciton band. This law is determined by the

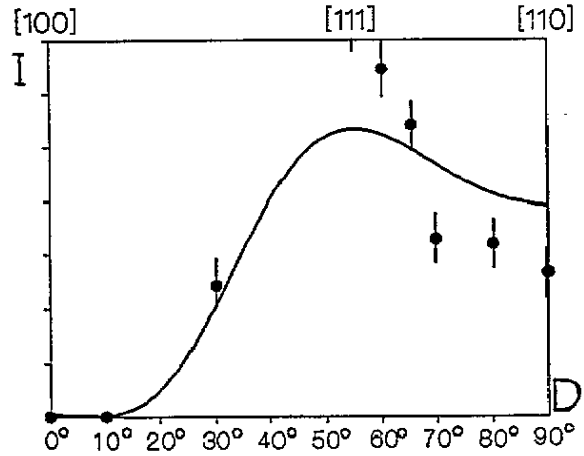

Figure 1. Inelastic form factor $I(Q)$ against angle between Q and the [100] direction. Experimental points are taken from [13]; the theoretical curve is calculated using equation (7) (see the text).

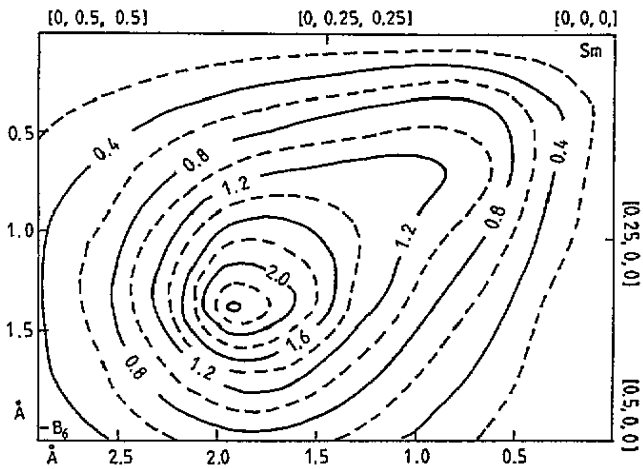

Figure 2. Relief of the electron density distribution for the model trial function in the plane [100]–[011]. The points [0, 0, 0] and [0.5, 0.5, 0.5] correspond to the Sm ion and the centre of the B_6 octahedron, respectively.

overlap integral of the wave functions B_m (3) centred on the neighbouring Sm sites. The Sm ions in SmB_6 form a simple cubic sublattice. In accordance with the above results for the charge density distribution (see figure 2) we assume that the boron p electrons give the main contribution to the 'tail' of the wave function B_m. Then calculating the indirect Sm–Sm overlap integrals via boron sites we find that three coordination spheres of the Sm sublattice with practically the same Sm–B–Sm bond lengths give the contribution to this overlapping. Therefore we assume in our calculations that the same overlap parameter W can be used for the first-, second- and third-neighbouring sites in the Sm sublattice. Within this approximation the dispersion law has the form

$$E(q) = E_{ex} + WS(q) \tag{9}$$

where $S(q)$ is a structure factor in a tight-binding approximation including the three coordination spheres mentioned above with a single overlap parameter W. This dispersion

law is presented in figure 3 for three principal directions of the Brillouin zone. It is seen that our calculations reproduce the main qualitative result of experimental studies [14]: the *minimum of the dispersion law in the [011] direction is shifted from the boundary point M,* whereas the boundary point R corresponds to the bottom of the exciton band in the [111] direction.

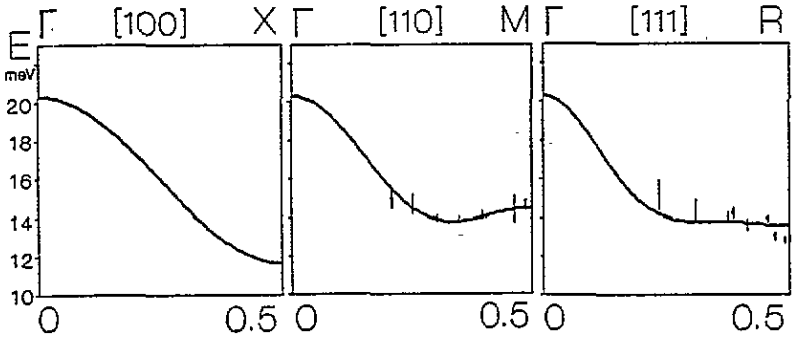

Figure 3. Calculated curves for the dispersion $E(q)$ of the exciton band for the values of $E_{cx} = 14$ meV, $T = 0.239$ meV. The experimental points are taken from [14].

Another unusual property of the inelastic peak in the spin scattering studied in [13, 14] is its temperature dependence: the peak is very narrow at low temperature, but drops very fast and broadens within the temperature interval 20–40 K. We think that this effect can be ascribed to the exchange interaction between the magnetic exciton and the thermally activated conduction electrons because it is known [15] that only at 20 K $< T <$ 40 K *the sign of the Hall coefficient of* SmB_6 *changes due to the appearance of the electrons* in a conduction band. We postpone the detailed calculation of the broadening of magnetic excitations for future publication, and here we only note that the possibility of obtaining a strong temperature decay of the inelastic peak due to a similar relaxation mechanism has been demonstrated for the CEF-split spectra in Ce-based Kondo lattices (see, e.g., [16]). Apparently, the rapid decay of the inelastic peak should be accompanied by appearance of the quasielastic scattering due to the same mechanism. Up to now we have available neither good experimental results for small frequencies nor adequate theory for describing such relaxation, so we leave this problem for future investigation.

It is instructive that the peaks with $\hbar\omega = 40$ meV corresponding to the intermultiplet transitions $^7F_0 \rightarrow ^7F_1$ within the $|4f^6\rangle$ Sm^{2+}-like configuration and $\hbar\omega = 120$ meV corresponding to the $^6H_{5/2} \rightarrow ^6H_{7/2}$ transition within the $|4f^5\rangle$ configuration of Sm^{3+} are also seen in the neutron scattering spectrum [17]. The widths of these peaks ($\Gamma/2 \approx 10$ meV are noticeably larger than those in compounds with strictly divalent or trivalent Sm. This broadening means that the transitions $f^6_{J=0\rightarrow J=1}$ and $f^5_{J=5/2\rightarrow J=7/2}$ persist in the IV state as resonances, i.e. as the non-eigenstates in the energy spectrum of the IV semiconductor. The presence of such excitations shows that the inelastic-neutron-scattering measurement is a fast process in comparison with the frequencies τ^{-1} of the valence fluctuations, so that both f^6 and f^5 instantaneous states of the Sm ion can be 'snapshot' along with the true exciton eigenstate (5), provided the measurement time is shorter than the dwelling time of the f^* electron in each valley of the double-well potential. However, the widths of these resonances should exceed substantially that of the state (5), and experiment confirms this conclusion.

3. Concluding remarks

We have found that the study of magnetic inelastic scattering in the singlet-state IV semiconductor gives us a unique opportunity to study the spatial distribution of electronic density in the ground and excited states by neutron-scattering methods. Its main features are the strong anisotropy and large spatial extension of this density which is reflected in a Q dependence of magnetic form factor and in characteristic dispersion of magnetic excitations. It should be noted that the low-energy magnetic excitations of IV SmB_6 were described a decade ago by Czycholl within a simple two-band alloy-analogy approximation with on-site fd hybridization [18]. The origin of the inelastic peak in his theory is connected with the interband but on-site contribution of f electrons to the spin–spin correlation function. Such a treatment cannot reproduce the actual anisotropy of $I(Q)$.

We emphasize once more that the specific spatial extension of the wave function $B_m^{(f)}$ (3) can be considered as a 'fingerprint' of the IV state. Another possibility of forming the IV state is pointed out by Kasuya and co-workers (see, e.g., [4, 19, 20]). They argue that the second term describing the screening of the valence fluctuation by the d electron should be added to the wave function (2). This term has the form

$$|f^5 df^* \bar{d}^*) = |f_m^5 f^* B_m^*(f)\bar{B}_m^*(d)). \tag{10}$$

Here d_m stands for the d electron created on the Sm site and $\bar{d}_m^* \equiv \bar{B}_m^*(d)$ describes the hole of d symmetry expanded over the neighbouring boron sites. Such a type of screening was shown previously to be effective in the photoemission processes in metallic Ce monopnictides, and now these electron–hole pairs of d symmetry are offered for a description of the ground state and low-energy excitations in semiconducting Sm-based compounds with narrow energy gaps. Kasuya and co-workers also claim that the variational function (2) with the added contribution (10) can result in inhomogeneous mixed-valence state with alternating di- and trivalent Sm ions, so the gap in the energy spectrum is induced by the intersite Coulomb interaction (as in the excitonic model described here).

It seems, however, that this mechanism has no definite confirmation either in the lattice properties or in the neutron-scattering spectra of Sm hexaboride. First, it is easily seen that the state (10) describes two interacting dipoles with different spatial distribution of the charge density. Such interaction should result in forming at least the quadrupolar momenta around each Sm site, and, hence, in cooperative Jahn–Teller-like ordering which is not seen in SmB_6 (cf. the ferroelectric ground state obtained for the 'essentially localized' model of on-site f–d valence fluctuations offered many years ago [21]). Second, the trial wave function (10) gives a form factor $G(Q)$ which differs essentially from (7) and strongly modifies the form factor of the phonon renormalization by valence fluctuation processes [10]. Both these factors obtained by means of the trial wave functions (3)–(5) give a good qualitative and quantitative description of the neutron-scattering experiments. Additional local modes in the vibrational spectrum of SmB_6 can also be explained in all details via the concept of the excitonic dielectric [22]. Thus we think SmB_6, like gold SmS, can be treated as an excitonic-dielectric-like semiconductor rather than as a low-carrier-density metallic system of Kondo type.

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