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STUDY OF THE ELECTRONIC STRUCTURE OF ALUMINUM COMPOUNDS
WITH 3d-TRANSITION METALS

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Compounds of Al with 3d-transition metals with structures of the CsCl variety have a whole series of unique properties: the magnetic properties of FeAl, the high melting temperature of NiAl, properties related to the shape memory effect, increased hardness, etc.

Experimental and theoretical research into the electron properties (kinetic and optical) of compounds of aluminum with one of the transition elements permits one to suggest that the peculiarities in these compounds are caused by their electron structure. Theoretical investigation of the energy band structure of the FeAl, NiAl, and CoAl compounds was done in [1-4].

Calculation of the integrated characteristics of the electron structure, such as the density of states, the kinetic and optical coefficients, etc., requires knowledge of the electron energy spectrum at a large number of points of a Brillouin zone (BZ); therefore, it is most effective to use an interpolation model of the electron structure.

This work, which to some degree has a methodological character, based on a model Hamiltonian, calculates the energy spectrum, the density of states, the valence electron population numbers of different atomic orbitals, and the electron specific heat capacity. In addition, the kinetic stability of the FeAl, NiAl, and CoAl compounds with CsCl type structure is confirmed. It is shown that using the interpolation method for calculating the electron structure makes it possible to compute, relatively accurately in comparison with experimental data and calculations from first principles, the integrated characteristics of the electron structure and to predict the electrophysical properties of aluminides.

The equation for the eigenvalues of the band Hamiltonian has the form:

$$H\Psi_{\kappa n}(r) = E_n(\kappa)\Psi_{\kappa n}(r). \tag{1}$$

The model basis functions $\Psi_{\kappa n}(r)$ (n is the energy band index) are taken in the form of a sum of symmetrized linear combinations of orthogonal plane waves (OPW) $\Phi_{\kappa_j}(\kappa, r)$ and linear combinations of Bloch functions of the 3d-electrons $\chi_\mu(\kappa, r)$ (strong coupling approximation)

$$\Psi_{\kappa n}(r) = \sum_{K_i} a_{nK_i}(\kappa)\Phi_{K_j}(\kappa, r) + \sum_\mu a_{n\mu}(\kappa)\chi_\mu(\kappa, r). \tag{2}$$

Here the summing is done over inverse lattice vectors with components (in units of $2\pi a$, a is the lattice constant) (0, 0, 0), (1, 0, 0), (0, 1, 0), (1, 1, 0), (1, 0, 1), (0, 1, 1), (1, 1, 1) and over all population states with T_{2g} ($\mu = 1, 2, 3$) and E_g ($\mu = 4, 5$) symmetries of the orbitals in the irreducible 1/48 part of the BZ; $a_{nK_i}(\kappa)$, $a_{n\mu}(\kappa)$ are the linear combination coefficients.

The eight OPW describing the s-type band have the form

$$\Phi_{K_j}(\kappa, r) = C^{-\frac{1}{2}}(e^{i(\kappa-K_j)r} - \sum <\chi_\mu(\kappa, r)|e^{i(\kappa-K_j)r}> \chi_\mu(\kappa, r),$$

where C is the normalization factor.

The Bloch functions of the 3d-electrons are taken in the form

$$\chi_\mu(\kappa, r) = <r|\kappa\mu> = N^{-\frac{1}{2}}\sum_l e^{i\kappa R_l}\varphi_\mu(r - R_l),$$

$\varphi_\mu(r - R_l)$ is the atomic 3d-orbital centered at the point R_l (R_l is the translation vector of a given crystal lattice).

The matrix corresponding to the band Hamiltonian and calculated from the basis wave functions of Eq. (2) has dimensions 13 × 13 and consists of OPW (8 × 8 submatrix), d–d (5 × 5 submatrix) and hybridized blocks which describe the conductivity band, d-type band, and the hybridization effects, respectively.

The expression for the matrix elements of the OPW block is taken from [4].

$$<\Phi_{K_i}(\kappa, r)|\hat{H}|\Phi_{K_j}(\kappa, r)> = \alpha|\kappa - K_i|\delta_{ij} + [F_{K_i}(\kappa)\cdot F_{K_j}(\kappa)].$$

$$\times (1 - \delta_{ij}) + \delta_{ij}\{V_{|K_i-K_j|} + S\cdot J_2(\kappa - K_j|R)\cdot J_2(|\kappa - K_i|R) \times \quad (3)$$

$$\times P_2[(\kappa \overset{\frown}{-} K_i)(\kappa \overset{\frown}{-} K_j)]\}.$$

Here $J_2(x)$ is a second-order spherical Bessel function; $P_2(\kappa, \overset{\frown}{K})$ is a Legendre polynomial for $\ell = 2$; $V_{|K_i=K_j|}$ are the Fourier components of the local pseudopotential; α, R, S are the interpolation parameters; and $F_{K_i}(\kappa)$ are the symmetrization factors. The last term in Eq. (3) is stipulated by the orthogonalization of the plane waves to the Bloch sum of 3d-symmetry and can be interpreted as a nonlocal dependence on the κ pseudopotentials.

The matrix elements of the d–d block are taken in the form [5]

$$<\chi_\mu(\kappa, r)|\hat{H}|\chi_{\mu'}(\kappa, r)> = \sum_{R'_s} e^{i\kappa R'_s}E_\mu(R'_s), \quad (4)$$

where $E_\mu(R'_s)$ are the integrals of the overlap of the pseudopotential of the crystal field in the lattice. When calculating the overlap integrals, the energy of splitting by the crystal field in the lattice of the energy of the 3d-electrons in the center of the BZ is taken into account.

The nondiagonal elements of the band Hamiltonian matrix (5 × 8 submatrix)

$$<\chi_\mu(\kappa, r)|\hat{H}|\Phi_{K_j}(\kappa, r)> =$$
$$= B_2 J_2(|\kappa - K_j|R)\cdot Y_{2\mu}(\kappa - K_j) \text{ for } \mu = 1, 2, 3 \ (T_{2g}\text{- orbital}), \quad (5)$$

$$= B_3 J_2(|\kappa - K_j|R) Y_{2\mu}(\kappa - K_j) \text{ for } \mu = 4, 5 \ (E_g\text{- orbital}),$$

are the matrix elements between the orthogonal plane waves and the Bloch functions. Here B_2, B_3 are the hybridization parameters and $Y_{2\mu}(\kappa - K_j)$ are spherical harmonics.

The numerical values of the overlap integrals $E_\mu(R'_s)$ are determined as the parameters from the energy spectra of the nonhybridized 3d-levels, where the formulas for the matrix elements of the d–d block are highly simplified. Here in Eq. (4) the integrals for the neighboring two closest coordination spheres are retained. The parameters of the conduction band α, R, S are fitted for points closest to the peaks of the energy band, allowing for the spectrum of the conductivity electrons not to be shifted with the spectrum of the 3d-levels. The hybridization parameters are selected such that they correctly, as for calculations from first principles, describe the hybridization at points of high symmetry. The accuracy of the calculated eigenvalues of the band Hamiltonian reached 0.02 Ry.

Figure 1 shows the energy spectra of the FeAl, NiAl, CoAl compounds with the CsCl crystalline lattice structure along the BZ symmetry directions Γ–Δ–x. The most important characteristics of the spectrum are shown in these figures. It is clear that the band structure of these compounds is characterized by the width of the s–p-conductivity band, which intersects the narrow 3d-band genetically related with the 3d-band of the transition metal. In going from FeAl to CoAl and then to NiAl, the center of the 3d-band (characterized by the resonance energy E_{3d}) drops.
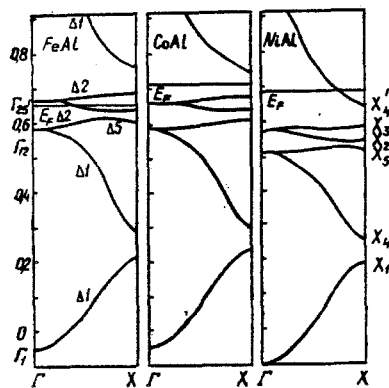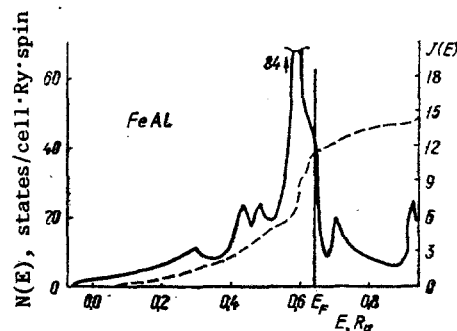
Fig. 1

Fig. 2

To clarify the features of the electron structure of the examined compounds, the density N(E) and number J(E) of states are respectively calculated according to the formulas:

$$N(E) = \frac{1}{\Omega} \sum_n \int_\Omega \delta\left(E - E_n(\kappa)\right) d\kappa, \tag{6}$$

$$J(E) = \frac{1}{\Omega} \sum_n \int \Theta\left(E - E_n(\kappa)\right) d\kappa, \tag{7}$$

where Ω is the volume of the BZ, $\Theta(x) = \begin{cases} 1, & x \geq 0 \\ 0, & x < 0 \end{cases}$. The integration over the BZ in Eqs. (6) and (7) is done using the combined tetrahedral method [6]. For this, a calculation was first done on the energy spectra of the 3d- and s-p-electrons at 165 points of 1/48 part of the BZ on a homogeneous network of values. The statistical error in calculating the integrals in Eqs. (6) and (7) does not exceed 2%.

Figures 2-4 show the results of calculating the total densities and number of states of the valence electrons. The bottom of the conductivity band E_0 is taken to be the energy reference (zero level). The vertical line shows the location of the Fermi level. It is clear from these graphs that the density of states has a complex structure and consists of a series of maxima of different intensity in which the total density of states is primarily determined by the partial density of the 3d-states of the transition metal while the numerical values of the chief maximum are characteristic for electrons of T_{2g}-symmetry.

The calculations showed that electrons of E_g-symmetry are distributed of T_{2g}-symmetry and occupy a greater energy interval. The 3d-bands of the examined compounds are completely filled since the integrated density of electron states ($\int N(E)dE$) higher than the Fermi level is negligibly small in comparison with the integrated density of states below the Fermi level. For the NiAl compound, Figure 3 shows as a dot-dash line the experimentally obtained curve for the density of states [7]. As follows from the comparison, the accuracy of calculating the electron structure of the examined compound by the interpolation method is found to be in satisfactory agreement with the experimental data and is comparable with the accuracy of calculating from first principles [8].
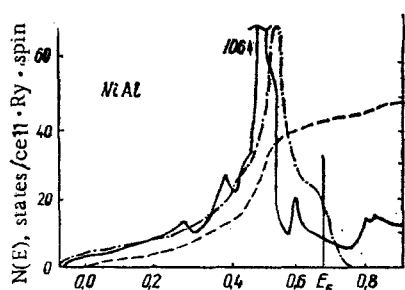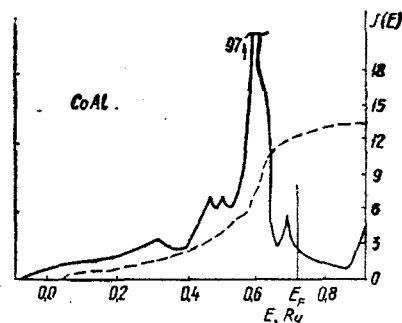

Fig. 3

Fig. 4

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TABLE 1

		FeAl	CoAl	NiAl
E_F		0,64	0,71	0,68
$N(E_F)$		38,4	12,2	8,72
γ		$6,51 \cdot 10^{-3}$	$2,09 \cdot 10^{-3}$	$1,41 \cdot 10^{-3}$
γ_{exp}		$5,447 \cdot 10^{-3}$ [2]	—	—
Population number of the orbitals	T_{2g}	4,74	5,88	5,94
	E_g	4,0	4,0	4,0
	$3d$	8,74	9,88	9,94
	OPW	2,26	2,12	3,06
Total number of valence electrons		11	12	13

The Fermi level of the FeAl compound enters into the decline in the chief maximum. For NiAl and CoAl, the Fermi level is already at the minimum of the density of electron states.

The obtained values of the Fermi energy (in units of Ry), and density of states at the Fermi level (in units of the number of electron states/cell·Rydberg), and the calculated values of the electron specific heat capacity γ (in units of J/mole·K^2) for the studied compounds are shown in Table 1.

On the basis of the calculated numbers of electron states and Fermi levels, we obtained the valence electron population numbers of compounds of transition metals with aluminum of different atomic orbitals from the bottom of the conductivity band up to the Fermi level. From Table 1 it follows that whereas in free atoms of transition metals Fe, Co, Ni the number of the 3d-electrons respectively equals 6, 7, and 8, for an atom of Al there are none at all. In a condensed state (on forming a compound), due to the effects of overlap of the bands, part of the 3s-, 3p-, and 4s-electrons of the atoms being alloyed is redistributed into the 3d-sublevels of the transition metal.

The author of [9] examined the question regarding the stability of compounds with structure of the transition-metal variety to external action (pressure, temperature changes). The author found the conditions for the existence of a stable compound with the given structure and the conditions which violate this existence. The conditions directly include the single electron band characteristics. It was established that the most favorable condition for the stability of the compounds is having E_F located in the wide gap in the density of states curve. The greater the value of $\delta = \Delta/N(E_F)$ (Δ is the width of the gap in which E_F is located), then the wider the stability region is for the given compound. Having calculated the width of the gap Δ in the density of states curve at the Fermi level and the parameter δ (FeAl: $\delta = 0.001$; CoAl: $\delta = 0.02$; NiAl: $\delta = 0.025$), we found that, in correspondence with [9], the stability of the studied compounds, i.e., transition-metal—aluminum, increases with increasing parameter δ.

Thus, it can be concluded that the interpolation model makes it possible to calculate the electron structure of compounds of Al with transition metals and to predict their electrophysical properties on this basis.

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