Conduction-electron contribution to the crystal potential in intermetallic compounds of rare-earth metals

E. A. Goremychkin and É. Myule
Joint Institute for Nuclear Research

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The parameters of the crystal electric field in intermetallic compounds of the type RNi_5 (R = Tb, Ho, Er) have been measured through the inelastic scattering of thermal neutrons. The difference between the values found for the parameter A_2^0 by neutron spectroscopy and the method of perturbed $\gamma - \gamma$ angular correlations is interpreted as an exchange contribution of conduction electrons to the crystal field.

Experiments have been carried out over the past decade on the crystal electric field in compounds with a cubic point symmetry of an ion of a rare-earth metal by the method of inelastic scattering of thermal neutrons. These experiments have yielded contradictory results on the role played by conduction electrons in forming the crystal electric field.[1,2]

It has also been demonstrated that the model of effective point charges is not adequate in the case of metallic systems. Since the crystal field largely determines the properties of compounds of rare-earth metals, the nature of the crystal field in a metal is one of the central problems in research on compounds of rare-earth metals.

A phenomenological model of the crystal field with a Hamiltonian[3]

$$\mathcal{H} = \sum_{l \leqslant 6} \sum_{m=-l}^{+l} A_l^m \langle r^l \rangle \Theta_l O_l^m (J_+, J_-, J_z, J) \qquad (1)$$

is used to interpret the properties of compounds of rare-earth metals; here the O_l^m are equivalent Stevenson operators, the A_l^m are empirical parameters of the crystal field, which are determined from experiments on the inelastic scattering of thermal neutrons, the $\langle r^l \rangle$ are radial integrals,[4] and Θ_l is the Stevenson factor.

In this letter we report measurements of the inelastic scattering of thermal neutrons by samples in which an ion of a rare-earth metal has a hexagonal point symme-

TABLE I.

Compound	A_2^0	A_4^0	A_6^0	A_6^6
$HoNi_5$	− 216	− 16.7	5.2	151
$TbNi_5$	− 138	− 9,8	5.9	190
$ErNi_5$	− 108	− 44,3	9,1	52,1

The error in the parameter A_2^0 is ~3%, while that in A_4^0, A_6^0, and A_6^6 is ~10%.
The dimensions the A_l^m are meV/Å^l.

try: RNi_5, where R = Tb, Ho, or Er (the $CaCu_5$ structure). We used a time-of-flight spectrometer in the inverse geometry with a beryllium filter in front of the detector in the IBR-30 reactor of the Neutron Physics Laboratory of the Joint Institute for Nuclear Research. We used the method of Ref. 5 to determine four parameters of the Hamiltonian of the hexagonal crystal field from the neutron scattering spectra; these parameters are given in Table I. The parameters A_l^m do not depend on the particular nature of the rare-earth ion; they are determined exclusively by the crystal field produced by the surroundings of this ion in the crystal. An unexpected result regarding the parameters A_l^m is that they are significantly different in isostructural compounds with similar lattice constants, showing no tendency toward a regular change except in terms of the sign.

The differential perturbed $\gamma - \gamma$ angular correlations were measured in Ref. 6 for the group of compounds RNi_5 (R = Pr, Nd, Tb, Dy, Er), and the results were used to determine the gradients of the crystal field at the position of the nucleus of the rare-earth ion. The parameter A_2^0 found in the neutron experiments is actually the gradient of the crystal field at the position of the $4f$ electron shell of the rare-earth ion, averaged over the radial part of the wave function. The gradient of the crystal field, V_{zz}, is related to the parameter A_2^0 by

$$V_{zz} = -\frac{4A_2^0}{e}. \tag{2}$$

In a recent study[8] of a large number of nonconducting compounds RF_3, we showed that the gradients of the crystal field at the nucleus of the rare-earth ion and at its $4f$ shell are identical. The first column of Table II gives the values of A_2^0 for metallic systems determined from the inelastic scattering of thermal neutrons and measurements of the magnetic properties of single crystals.[7] In other words, these results were found from the reaction of the $4f$ electron shell to the crystal field. The second column shows the values of A_2^{0*}, which were calculated from the gradient of the crystal field at the nucleus of the rare-earth ion, V_{zz}, in accordance with (2) (Ref. 6). Comparison of the values of A_2^0 and A_2^{0*} in Table II shows that there is a large difference between the gradients of the crystal field at the nucleus and at the $4f$ electron shell. The ratio of these gradients in the case of $PrNi_5$ is ~6, while that for the other RNi_5 compounds is ~3.

The good agreement between the gradients of the crystal field at the nucleus and the $4f$ shell in the case of insulators and the large difference between these gradients in

TABLE II.

Compound	A_2^0	A_2^{0*}	$A_2^0 - A_2^{0*}$
$PrNi_5$ [1)]	− 67.6	454	− 521
$NdNi_5$ [2)]	− 144	448	− 592
$TbNi_5$	− 138	436	− 574
$DyNi_5$ [2)]	− 143	441	− 584
$ErNi_5$	− 109	439	− 547

[1)]Data of Ref. 10; the error in A_2^0–A_2^{0*} is ~5%.
[2)]Data of Ref. 7; the dimensions are meV/Å^2.

the case of metallic compounds appears to us to result from an important effect of conduction electrons on the crystal field in metals. According to a suggestion by Devine and Berthier,[9] the total quantity A_2^0 can be written as the sum of three terms:

$$A_2^0 = (A_2^0)_1 + (A_2^0)_2 + (A_2^0)_3 , \quad (3)$$

where $(A_2^0)_1$ is the component of the crystal field due to the ion cores (ligands), $(A_2^0)_2$ is the direct Coulomb contribution from conduction electrons, and $(A_2^0)_3$ is the exchange contribution of the conduction electrons. The $4f$ electron shell is affected by all three components of the crystal field, while the nucleus is affected by only the first two components, so that the difference between A_2^0 and A_2^{0*} can be attributed to the exchange contribution from conduction electrons (the third column in Table II).

The most important result of this study is the demonstration that conduction electrons in metallic compounds contribute substantially to the gradient of the crystal electric field, and measurements of the electrostatic part of the hyperfine interaction and of the inelastic scattering of thermal neutrons provide a method for experimentally identifying the exchange contribution of conduction electrons to the gradient of the crystal electric field.

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