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Densities of States and Calculated *K* X-Ray Spectra of TiFe

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Densities of states and *K* x-ray emission and absorption spectra from both components of a 50-50 intermetallic compound TiFe were calculated using results of self-consistent energy-band calculations. The calculated x-ray spectra agree well with experiment.

In recent years, self-consistent band calculations have been performed for many monatomic materials and some compounds in which only one component is a transition metal.[1] Several x-ray emission spectra and a few absorption spectra[2] have also been computed using the results of non-self-consistent band calculations.

In the present work the augmented plane-wave method (APW)[3] of band theory was employed to calculate, self-consistently, the energy bands and wave functions of an intermetallic compound between the 3*d* transition elements Ti and Fe. Slater's $X\alpha$ method[4] was used to approximate the exchange potential, with the α values calculated by Schwartz.[5] The results were subsequently used to obtain the x-ray spectra involving the 1*s* (*K*) level.

This is the first time that emission and absorption spectra have been calculated for both sites in an alloy. Comparison of calculated and measured spectra provides a test of the theoretical, local, component densities of states over a wide energy range.

The APW calculation was carried out at 512 points in the simple cubic Brillouin zone. Eigenvalues and the electronic charges[6] within the APW spheres were then interpolated[7] by Monte Carlo sampling of 96 000 points in the zone, and the *s*-, *p*-, and *d*-like densities of states (DOS) were obtained for both the Ti and the Fe sites.

Figure 1 shows the total DOS and its two *d* components. We observe the low DOS at the Fermi level characteristic of a paramagnetic material[8] and consistent with electronic specific heat measurements.[9] We also observe that, as one might have expected,[10] the heavier element (Fe) has larger local DOS below the Fermi level, while the lighter element (Ti) yields larger local DOS above the Fermi level. Figure 2 shows the *s*- and *p*-like DOS which are, typically for transition metals, much smaller than the *d*-like DOS. (Note a factor of 10 difference in our scale for Figs. 1 and 2.)

In order to obtain x-ray spectra from the above component DOS we form their products with the

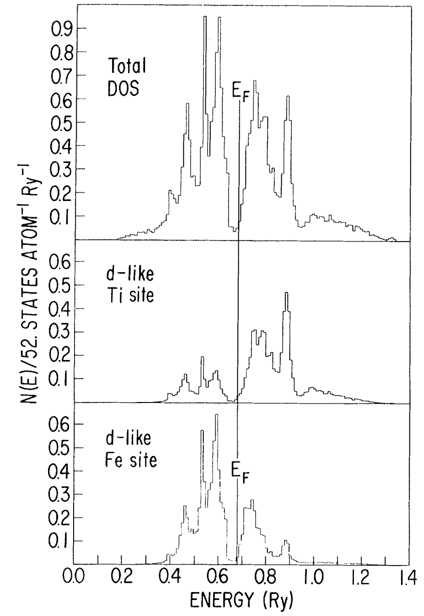

FIG. 1. Total and *d*-like densities of states of TiFe.

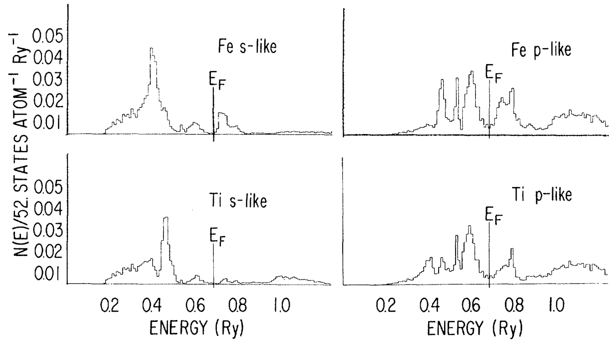

FIG. 2. s- and p-like densities of states for both sites of TiFe.

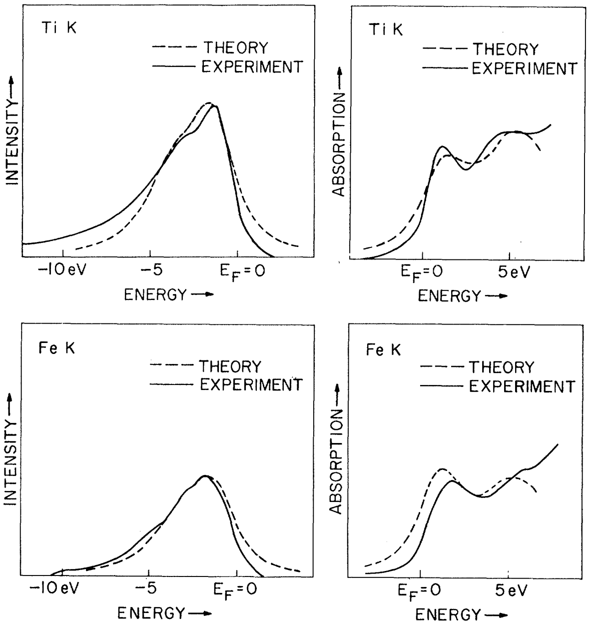

FIG. 3. K emission and absorption spectra for both sites of TiFe. Solid line, experiment (Ref. 9). Dotted line, present results.

radial transition probability.[2] In particular, according to the dipole approximation, the K spectrum will be the product of the p-like DOS and the probability of transition to the $1s$ state from the occupied band for emission spectrum and to the unoccupied band for absorption spectrum. Finally, the calculated spectra were broadened by an energy-dependent Lorentzian function which included a spectrometer distortion function of 0.03 Ry, a core broadening of 0.08 Ry, and electron lifetime broadening of the form $0.25(E-E_F)^2$, where E is the band energy and E_F the Fermi level.

Figure 3 shows the K emission and absorption spectra of both sites in TiFe, compared to the data of Nemnonov and Kolobova.[11] The spacing and relative intensity of peaks in the computed spectra reflects details in the p-like DOS shown in Fig. 2. The emission spectra are in generally good agreement with experiment. The absorption spectra show that the spacing between peaks in the density of empty p-like states was correctly obtained, but the high-energy peak is somewhat too low in amplitude. If the measured spectra contain the effects of a characteristic energy loss[12] of about 5 eV, the latter discrepancy would be explained.

In summary, a self-consistent energy-band calculation for an alloy between two transition metals has been performed.[13] The results were checked by computation of the K x-ray spectra and a comparison with experiment. Although there are differences in detail, the overall agreement is good. The small discrepancies between theory and experiment may be attributed to the local nature of the K orbital (the small region in the unit cell probed by K spectra), or to the interpolation scheme[7] used to obtain the densities of states. In addition, since both the $1s$-core and the valence-band wave functions were calculated with the $X\alpha$ exchange, the results indicate that this approximation produces better core states than one would expect.

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Reduction Factors for the Jahn-Teller Effect in Solids

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In the linear Jahn-Teller effect of an electronic E state, we report on the distinction between coupling with one set of doubly degenerate vibrational modes, and coupling with several such sets of different frequencies (the multimode Jahn-Teller effect) as is the case for an impurity in a solid. Whereas the combination of the reduction factors $2q-p$ is exactly unity in the former case, it is shown to be less than unity in the latter. Also, the value of q may decrease below $\frac{1}{2}$.

The concept of reduction factors[1] has greatly advanced the experimental verification of the Jahn-Teller effect.[2] Theoretically, the case $E \otimes \epsilon$ (an electronic E state coupled vibronically with a single pair of ϵ-type vibrational modes) has been thoroughly studied, and it has been shown that for weak to moderate Jahn-Teller coupling the vibronic ground state remains doubly degenerate. The vibronic coupling will then show up experimentally by the reduction in the values of various perturbations which split the ground-state doublet.

A simple way of measuring the reduction is in EPR, from the anisotropic part of the g factor which is given (apart from a known numerical constant) by $q\lambda/\Delta$. Here λ is a spin-orbit coupling constant which is either independently determined or estimated from the value on the free ion, Δ is the crystal-field splitting directly read off from optical spectra, and q is a reduction factor smaller than unity. Another reduction, symbolized by p, is encountered in the combined effect of applied magnetic field and trigonal strain. By comparing the measured values of the reduction factors with those evaluated from theoretical models, direct contact can be made between theory and experiment.

For linear coupling of arbitrary strength with a single pair of modes, the following relation holds between the reduction factors p and q [defined below in Eq. (5)]:

$$2q-p=1 \quad (\text{for } E\otimes\epsilon). \tag{1}$$

Under the same conditions it has been shown that $1>q>0.5$, with a slight decrease in the lower limit (0.484) when higher-order terms in the coupling are included.[3] Up to the present these results have been accepted without reservation,[4] and experiments have been interpreted in terms of q taking values down to about $\frac{1}{2}$.[1,2] Exceptional is a value $q=0.2$ obtained for Cu^{+2} in MgO.[5]

Realistically, for impurities in solids the vibronic coupling is with several sets of modes. We shall show that the equality in Eq. (1) is a rather special case valid for coupling with a single pair of modes, whereas for the multimode Jahn-Teller effect, $E\otimes\sum_i\epsilon_i$, the relation which in general holds is

$$2q-p<1 \quad (\text{for } E\otimes\textstyle\sum_i\epsilon_i). \tag{2}$$

In the latter case q may be significantly reduced below $\frac{1}{2}$, and, in fact, for coupling with two sets of modes, as detailed below, a value as small as $q=\frac{1}{4}$ is possible. The emergence of this possibility poses a challenge to the experimentalists to confirm a value of q significantly lower than 0.5, a finding which has perhaps escaped them so far because of their reliance on accepted theoretical predictions. Additionally, p and q may be simultaneously measured and $2q-p$ evaluated. A result less than 1, according to the predictions of this Letter, may be due to linear coupling with many modes rather than to nonlinear coupling with one set of modes.

We consider the Hamiltonian

$$\mathcal{H}=\textstyle\sum_i\hbar\omega_i(\frac{1}{2}\vec{p}_i^{\,2}+\frac{1}{2}\vec{q}_i^{\,2}+k_i\vec{q}_i\cdot\vec{\sigma}). \tag{3}$$

Here $\vec{q}_i$ is a two-dimensional vector whose com-