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Electronic Band Structure of Niobium Nitride

L. F. Mattheiss
Bell Laboratories, Murray Hill, New Jersey 07974

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The augmented-plane-wave method is applied to calculate the electronic band structure of niobium nitride (NbN). The results are qualitatively similar to those obtained from previous energy-band calculations for the 3*d* transition-metal monoxides which form with the same rocksalt structure. The Fermi level for NbN falls in the lower portion of the t_{2g} manifold of the niobium 4*d* bands so that the conduction electrons in NbN are predominantly 4*d*-like in character. These results are compared with some of the previous band-structure models that have been proposed to explain the electronic properties of NbN and other closely related refractory hard metals with the rocksalt structure.

I. INTRODUCTION

Niobium nitride is one of a family of refractory "hard metals" that can be formed by combining boron, carbon, or nitrogen with Group-IV, -V, and -VI transition-series elements. These compounds are characterized by high melting points, hardness, brittleness, and resistivities comparable to those observed in good metals.[1] In addition, these compounds include materials with high superconducting transition temperatures, and these transition temperatures are found to vary significantly with composition.

Geballe *et al.*[2] have measured the superconducting transition temperatures, lattice parameters, low-temperature heat capacities, and magnetic susceptibilities of the niobium nitride-carbide system. They have found unusually small values for the electronic heat-capacity coefficient and the magnetic susceptibility in these compounds. This has led them to propose an energy-band model for NbN containing niobium 5*s*-5*p* and nitrogen 3*s*-3*p* electrons at the Fermi level, with the niobium 4*d* bands above the Fermi energy and therefore unoccupied.

A variety of band-structure models had been proposed previously to explain the physical properties of these materials. One of the original ideas was suggested by Hägg[3] about 40 years ago. Hägg proposed that these materials could be regarded as interstitial alloys rather than compounds, with the nonmetal atoms merely filling the voids in the host lattice of transition-metal atoms. As a result of this model, these materials are frequently referred to as "interstitial" compounds. This simple idea has been refined and improved over the years, and two distinct models have emerged.[1] The first model stresses the importance of metal-metal bonds in explaining the stability and other observed properties of these materials. The second model attributes these properties to the formation of metal-ligand bonds. As a refinement of the latter model, Bilz[4] carried out a simplified tight-binding calculation for TiC, TiN, and TiO using the Slater and Koster linear-combination-of-atomic-orbitals (LCAO) method.[5] He obtained a band-structure model in which the metal *s*-*d* and ligand *p* bands overlapped so that portions of these bands were partially occupied.

In order to test the validity of these models, the augmented-plane-wave (APW) method has been applied to calculate the electronic energy bands of stoichiometric NbN. These calculations produce a band structure in which the niobium 4*d* bands fall about 0.2 Ry above the nitrogen 2*p* bands. The Fermi level falls within the t_{2g} manifold of the niobium 4*d* bands so that the electric conductivity is due primarily to niobium 4*d* rather than niobium or nitrogen *s*-*p* electrons. The bottom of the antibonding niobium-nitrogen *s*-*p* band falls about 0.2 Ry above the NbN Fermi energy.

Very recently, Schwarz[6] has carried through a self-consistent APW calculation for NbN involving the Slater[7] $\rho^{1/3}$ approximation to the exchange potential that is applied here, but Schwarz has reduced this approximate exchange potential by the factor $\alpha = 0.7063$. He obtains energy-band results that are very similar to those obtained in the present calculation, except that the niobium 4*d* bands are lowered by about 0.3 Ry relative to the 2*p* bands so that the two manifolds overlap. Both these energy-band models for NbN are in qualitative agreement with Bilz's results. The main difference is that the APW results predict that the bottom of the metal *s*-*p* band is raised well above the Fermi energy. These APW results for NbN are rather similar to those which have been calculated previously by this method for the isoelectronic compound TiO, including the results of Ern and Switendick,[8] Schoen and Denker,[9] and the present author.[10] The present calculated NbN 4*d* bandwidth of 0.7 Ry is about 20% smaller than that obtained by Schwarz,[6] but is comparable with the 3*d* bandwidth calculated by Ern and Switendick[8] for TiO. It is about 40% larger than those obtained in the other calculations for TiO.[9,10] Each of these calculations predicts that the bottom of the antibonding *s*-*p* band is well above the Fermi level.

This is an important feature in the band structures of transition-metal compounds, one which distinguishes them from the transition metals. In the transition metals, it is well known that the *s*-*p* and *d* bands overlap so that both are partially occupied. This leads to strong hybridization effects, particularly in those energy ranges where the *s*-*p* and *d* bands are degenerate. In the transition-metal compounds, these hybridization effects are small compared to the overlap-covalency interactions which occur between the metal *s*-*p* and *d* and ligand *s*-*p* orbitals. The overlap and covalency between the metal *d* and ligand *s*-*p* orbitals produces crystal-field type interactions within the manifold of the metal *d* bands. Those *d*-band states for which the ligand-metal *s*-*d* or *p*-*d* interactions are small (or vanish because of symmetry) change only slightly in going from the metal to the compound. The main effect is a narrowing of the normal *d* bandwidth because of the increased lattice parameter in the compound. The remaining *d*-band states are shifted to higher energies by the *s*-*d* and *p*-*d* overlap and covalency effects, which increase *d* bandwidth until it is comparable with that in the metal.

A similar but stronger interaction occurs between the ligand and metal *s*-*p* orbitals. In this case, the overlap and covalency are considerably stronger because the metal *s*-*p* orbitals have larger radii than the *d* orbitals. In ReO_3, it has been shown[11] that these effects raise the bottom of the rhenium 6*s*-6*p* band by 0.6 Ry. In terms of the LCAO method, it can be shown that these effects are three times larger in the rocksalt structure.[10] According to this model, it is estimated that niobium-nitrogen *s*-*p* overlap and covalency effects raise the bottom of the niobium 5*s*-5*p* band by about 10 eV in NbN. Although this shifted band is more precisely described as an antibonding niobium-nitrogen *s*-*p* band, it will be frequently referred to here simply as the niobium 5*s*-5*p* band. These effects were neglected by Bilz[4] in his tight-binding calculation, and this led to a band structure in which the bottom of the metal *s* band fell several electron volts below the *d* band.

It has not yet been possible to prepare good single-crystal stoichiometric samples of NbN. The measurements of Geballe *et al.*[2] were carried out on samples whose compositions were $NbN_{0.91}$ and $NbN_{0.84}$, respectively. In addition to this lack of stoichiometry, it is also quite possible that these samples contain appreciable numbers of vacancies on both the niobium and nitrogen sublattices, since these are already known to exist in similar transition-metal compounds with the rocksalt structure.[12] These effects complicate the problem of relating the limited experimental data for NbN to the energy-band results. However, it is shown that these effects are not expected to change the prediction that the conduction electrons in NbN are primarily 4*d*-like in character.

II. RESULTS

The present APW calculation for NbN involves computational techniques which have been described

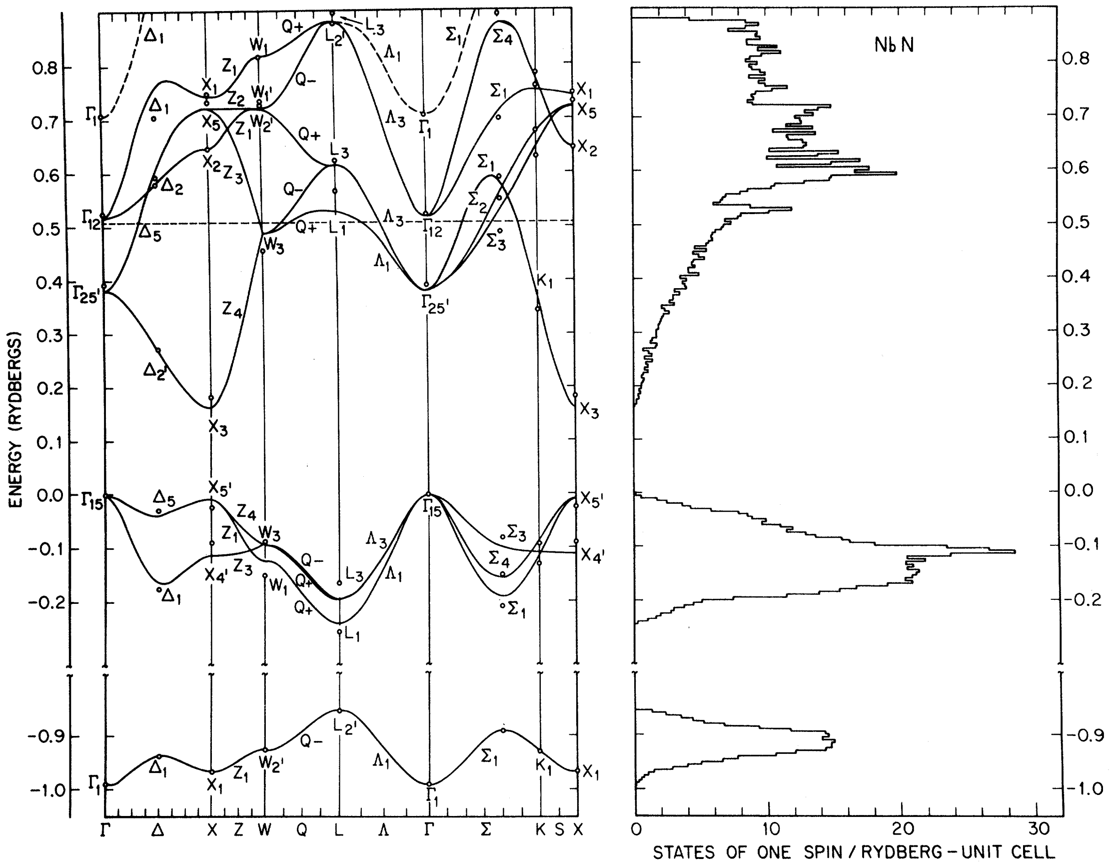

FIG. 1. Energy-band and density-of-states results for NbN.

elsewhere.[10] Although the lattice parameter for the niobium-nitrogen system varies with composition, the present calculation utilizes the value $a = 4.391$ Å that Geballe *et al.*[2] measured for their most stoichiometric sample $NbN_{0.91}$. The crystal potential for this calculation is obtained by a superposition of neutral-atom Hartree-Fock-Slater charge densities which are calculated by means of the Herman-Skillman self-consistent field program.[13] Slater's original method for approximating the exchange potential is applied.[7] The APW calculations are carried out at seven symmetry points in the fcc Brillouin zone, including the points Γ, X, L, W, K, Δ, and Σ. These APW results are used to determine 16 parameters in a simplified LCAO secular equation, which permits one to extend the energy-band results throughout the rest of the Brillouin zone by interpolation.[10]

The results of the APW and LCAO calculations for NbN are shown in Fig. 1. The solid lines are the LCAO bands and the open circles represent the APW results. The LCAO fit, which involves the nitrogen $2s$, $2p$ and niobium $4d$ orbitals, provides a fairly accurate representation of the NbN energy bands, although some obvious errors exist. The niobium $5s$-$5p$ bands are omitted from this LCAO interpolation calculation; the lower portions of these bands are drawn with dashed curves near the top of the figure.

The density-of-state curve to the right is obtained from the LCAO bands by sampling 108 000 uniformly distributed points in the fcc Brillouin zone. The contribution of the niobium $5s$-$5p$ bands is not included in this curve. The Fermi energy for stoichiometric NbN is indicated by the dashed horizontal line. It occurs within the t_{2g} manifold of the niobium $4d$ bands which originate from $\Gamma_{25'}$ at the center of the Brillouin zone. The e_g bands, which originate from Γ_{12}, are raised above the Fermi energy by a combination of nearest-neighbor $4d$-$4d$, $2s$-$4d$, and $2p$-$4d$ interactions. Similar but stronger interactions have raised the niobium $5s$-$5p$ bands so that Γ_1 is about 0.2 Ry above the Fermi energy. The bands at negative energies are associated with the nitrogen $2s$ and $2p$ orbitals, though the wave functions for these states are actually bonding combinations of nitrogen and niobium orbitals.

The LCAO parameters that are determined from the present APW results for NbN are listed in Table I. These parameters are defined in Table II

TABLE I. LCAO parameters for NbN. (Energy parameters are in rydbergs.)

Parameter	Present calculation	Schwarz
E_s	− 0.8541	− 0.8481
$(ss\sigma)$	− 0.0114	− 0.0148
E_p	− 0.0336	− 0.0739
$(pp\sigma)$	0.0201	0.0351
$(pp\pi)$	− 0.0061	− 0.0094
E_{xy}	0.4956	0.1847
$E_{3z^2-r^2}$	0.4584	0.1682
$(dd\sigma)$	− 0.0736	− 0.0773
$(dd\pi)$	0.0307	0.0286
$(dd\delta)$	− 0.0033	− 0.0005
S_s	0.0662	0.0718
$(sd\sigma)$	− 0.1733	− 0.1758
S_σ	0.1061	0.1152
$(pd\sigma)$	− 0.1512	− 0.1621
S_π	− 0.0277	− 0.0394
$(pd\pi)$	0.0694	0.0830
rms error	0.0168	0.0190
max error	0.0533	0.0695

of Ref. 10, where the LCAO matrix for the rocksalt structure is tabulated. Also included in this table are the corresponding parameters that have been determined from Schwarz's self-consistent energy-band results for NbN.[6] For convenience the zero of energy is adjusted prior to the LCAO fit so that $E(\Gamma_{15}) = 0$ in each case. In general, the agreement between the two sets of LCAO parameters for NbN is quite satisfactory. The main difference is that the 4*d* bands in Schwarz's calculation are lower in energy (relative to the top of the nitrogen 2*p* bands) by about 0.3 Ry. This is sufficient to cause the 2*p* and 4*d* bands to overlap, whereas the present model predicts an 0.2-Ry gap separating these bands. The rms and maximum errors in the LCAO fits to the APW results are listed at the bottom of Table I.

Although the LCAO interpolation method provides a good qualitative representation of the NbN band structure, it does introduce errors as large as 0.05 Ry. Some of these errors are reflected in the density-of-states curve of Fig. 1. The peak in the density of states just above the NbN Fermi level is due to such an effect. Analysis of the LCAO band structure indicates that this peak in the density of states arises from a flat band that connects $\Sigma_3[\vec{k} = (\pi/a)(1,1,0)]$ and $L_1[\vec{k} = (\pi/a)(1,1,1)]$ along the edges of a cube joining the eight L points in the Brillouin zone. While this band is flat to within 0.001 Ry in the LCAO calculation, the APW results at Σ and L predict a 0.075-Ry bandwidth. Thus, the sharpness of this peak in the density of states is due largely to inaccuracies in the LCAO bands, and this peak would be smeared out over ± 0.04 Ry if the density of states were determined directly from the APW results. This conclusion is consistent with Schwarz's calculation of the density of states for NbN[6] in which he applies the original Slater and Koster[5] form of the LCAO interpolation method to fit his energy-band results. His density-of-states curves exhibit no well-defined structure in the immediate vicinity of the Fermi energy.

The LCAO fit to the APW results for NbN could be improved in a number of ways. The largest errors are due to the fact that the niobium 5*s*-5*p* orbitals have been omitted from the secular equation. These states have a noticeable interaction with the nitrogen 2*s* and 2*p* as well as the niobium 4*d* states. The omission of these niobium 5*s*-5*p* orbitals from the secular equation causes some of the LCAO parameters to represent "effective" rather than "direct" interactions. For example, the parameters E_s and $(ss\sigma)$ are included in the LCAO secular equation as a nitrogen 2*s* orbital energy and a nearest-neighbor two-center 2*s*-2*s* interaction integral, respectively. These parameters actually contain a contribution of this type, but they also include an indirect contribution from overlap and covalency between the nitrogen 2*s* and niobium 5*s* orbitals. The magnitude of the *d*-*d* interaction parameters $(dd\sigma)$, $(dd\pi)$, and $(dd\delta)$ in Table I indicates that an improved fit to the 4*d* bands might require the inclusion of second-neighbor *d*-*d* interactions.

III. DISCUSSION

The *s*-*p* band model of Geballe *et al.*[2] for NbN was introduced to explain the small values that they measured for the magnetic susceptibility and the electronic heat-capacity coefficient. For the $NbN_{0.91}$ and $NbN_{0.84}$ samples, they obtain values for the heat-capacity density of states $N_\gamma = 0.56$ and 0.63 states/eV molecule spin, respectively. By extrapolation, they predict that $N_\gamma = 0.5$ states/eV molecule for stoichiometric NbN. The calculated density-of-states curve in Fig. 1 also suggests a small band density-of-states for NbN. These results predict that $N(0) = 0.54$ states/eV molecule for stoichiometric and defect-free NbN. This value is probably uncertain to within ± 10% because of the limited sampling that is involved in the calculation of the density-of-states curve. Schwarz's density-of-states curve yields approximately the same value for $N(0)$.[6]

According to a rigid-band model, nitrogen vacancies are expected to remove states from the 2*s* and 2*p* bands. This would add electrons to the niobium 4*d* bands, raise the Fermi energy, and (according to the results of Fig. 1) increase the band density of states at the Fermi level. However, one cannot trust a rigid-band model when it is applied to vacancies since the NbN conduction bands depend critically on nearest-neighbor niobium-nitrogen interactions. One can anticipate significant changes in the details of the density-of-states curves in situations where vacancies exist on either the niobium or nitrogen sublattices.

By means of a simple calculation, we can estimate the effect of nitrogen vacancies on the position of Γ_1, the bottom of the niobium $5s$-$5p$ band. If one assumes that there are no niobium vacancies in the compound $NbN_{0.84}$, then on the average, one of the six nitrogen atoms that normally surround a given niobium atom is missing. If there were no interaction between the niobium $5s$ and nitrogen $2s$ orbitals, it is estimated that the energy of Γ_1 would fall somewhere between 0.0 to 0.1 Ry on the energy scale of Fig. 1. For the rocksalt structure, the second-order shift in the energy of this Γ_1 state[10] is proportional to N^2, where $N=6$ (the number of nearest-neighbor nitrogen atoms) in stoichiometric NbN. Since on the average $N=5$ for $NbN_{0.84}$, the shift of Γ_1 would be reduced approximately by the factor $\frac{25}{36}$ or 70%. This would lower the energy of Γ_1 by 0.15 to 0.20 Ry in Fig. 1, placing it fairly close to the Fermi energy. At best, this could introduce a tiny pocket of antibonding s-p electrons at Γ, but their number would be small compared to the total number of niobium $4d$ electrons at the Fermi energy.

Nitrogen vacancies would have a similar effect on the antibonding portions of the niobium $4d$ bands. However, it is difficult to estimate their effect on the density of states at the Fermi level in a simple way.

Geballe *et al.*[2] have applied McMillan's procedure[14] to determine the band-structure density of states $N(0)$ and the electron-phonon enhancement factor $(1+\lambda)$ from their superconductivity and heat-capacity data. They find $\lambda \approx 1$ so that $N(0) \approx 0.24$ states/eV molecule for stoichiometric NbN. This "experimental" value for the band density of states is less than half the calculated value 0.54 states/eV molecule. However, there is considerable uncertainty in this experimental result. First, it is not known if vacancies exist at the niobium as well as the nitrogen sites in these nonstoichiometric samples. Furthermore, the experimental determination of N_γ is complicated by the fact that the plot of the heat-capacity data C/T vs T^2 is not linear above T_c. This introduces some uncertainty in the extrapolation to $T=0$, especially in these high T_c materials where one must extrapolate over a considerable temperature range to determine the intercept. For example, in the $NbC_{0.30}N_{0.70}$ system where $T_c = 17.38$ °K, a linear extrapolation would lead to a negative value for γ. Geballe *et al.*[2] point out that their determination of $N(0)$ and λ is also inexact because detailed experimental information on the NbN phonon spectrum is lacking. Finally, Testardi[15] has shown that for high-T_c superconductors, one does not obtain the correct density of states from the linear term in the specific heat, at least in the case of the A15 compounds. It seems quite likely that a similar effect is responsible for anomalous behavior of the specific-heat data in these niobium-nitride–carbide compounds.

In conclusion, the experimental data for NbN are quite limited, mainly because good, single-crystal samples are presently unavailable. In my opinion, the present $4d$-band model for the Fermi surface of NbN is consistent with the existing experimental data. Schwarz's energy-band model[6] for NbN also appears to be consistent with this data. It is concluded that NbN is an ordinary transition-metal compound, that its stability is determined by the formation of strong niobium-nitrogen bonds, and that the conduction electrons are primarily $4d$-like in character. It would be interesting to determine by means of optical or photoemission studies whether or not the nitrogen $2p$ and niobium $4d$ bands overlap in NbN. This information would provide a useful means for comparing the relative accuracies of Slater's original exchange approximation[7] and the more recent $X\alpha$ method,[16] provided that the band overlap in Schwarz's model is due to the $X\alpha$ method rather than self-consistency effects.

Note added in proof From recent heat-capacity data presented at the Stanford Conference on Superconductivity, Hulm and co-workers obtained a band density of states for $NbN_{0.90}$ which is only 8% smaller than the present theoretical result of 0.54 states/eV molecule for stoichiometric NbN [J. K. Hulm (private communication)].

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Probabilistic Treatment of Stepwise Energy Transfer and Infrared-to-Visible Conversion

H. J. Richter and R. K. Watts*
Institut für Angewandte Festkörperphysik der Fraunhofer-Gesellschaft,
Freiburg i. Br., Germany
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A probabilistic model for the two-photon process of infrared-to-visible light conversion by Yb^{3+}-Tm^{3+} or similar rare-earth ion systems in solids is considered. The model demonstrates the basic influence of the infrared pump power and the lifetime of the intermediate excited state on the conversion efficiency.

INTRODUCTION

The infrared-to-visible conversion of light by rare-earth ions has become known under the name Infrared Quantum Counter Action, and also under the acronym VISOR which stands for "visible from infrared by the summation of radiation."

In the numerous reports on this phenomenon, the double ion systems of type Yb^{3+}-Ho^{3+}, Yb^{3+}-Er^{3+}, or Yb^{3+}-Tm^{3+} excel among all investigated ions because of their high yields of infrared-to-visible conversion.[1–6] As host lattices transparent yttrium (or lutetium) compounds proved to be especially suited since Yb^{3+}, Ho^{3+}, Er^{3+}, or Tm^{3+} easily substitute for the Y^{3+} or the Lu^{3+} ion.

Auzel[1] traced the efficient mechanism of conversion to the stepwise, nonradiative energy transfer from Yb^{3+} to the second rare-earth ion of the system. His explanation was recently theoretically supported by Miyakawa and Dexter[7] and experimentally confirmed in several studies.[2–6] The coupling required for the nonradiative transfer is provided by multipolar or superexchange interactions.

If the energy transferred matches the energy accepted by the second ion the transfer is said to be resonant. In Fig. 1, a scheme of the two-step process for the nonresonant case is given. The excited Yb^{3+} ion may either transfer energy to the acceptor ion which is in the ground state and thus trigger the transition to the intermediate state, or it may transfer energy to one acceptor which is already in this intermediate metastable state and thus excite the upper state. The visible radiation is produced by the transition from the upper state to the ground state. When the transfer is nonresonant, the lattice acts as a sink for those phonons which are generated in the process of energy transfer because of the energetic mismatch between the energy-transferring and the energy-accepting ion.

Lattices which yield long lifetimes for the intermediate states of Ho^{3+}, Er^{3+}, or Tm^{3+} are preferable as hosts for double ion systems because the efficiency of the two-step process increases with the lifetime of the intermediate state.

The significance of this lifetime for the efficiency of the infrared-to-visible conversion was demonstrated by Guggenheim and Johnson[4] who found exceptionally long lifetimes for the ${}^5I_6$ state of Ho^{3+} and the ${}^4I_{11/12}$ state of Er^{3+} in BaLuF$_5$ and BaYF$_5$, while observing exceptional conversion efficiencies.

The model to be presented resembles the double ion system Yb^{3+}-Tm^{3+} in such hosts with respect to its basic principle as a converter of light; however, we do not want to stress this resemblance since we believe that the model as such is useful in revealing some general aspects of the nature of the two-step process. The model is introduced for the sake of simplicity only. Its adaptation to less simplified conditions is straightforward.

In the following the ion which is primarily responsible for absorbing and transferring photon energy will be called the donor or the "*D*" ion, and the ion which is responsible for the stepwise accumulation of energy will be called the acceptor or the "*A*" ion.

FEATURES OF THE MODEL

The model is based on five simplifications: (1) The pumping radiation is assumed to be matched to the absorption of the *D* ion, i.e., the *A* ion shall not participate in the absorption of infrared radiation; (2) the model is restricted to the two-photon process, i.e., excitations resulting from more than two stepwise energy transfers are neglected; (3) back transfer of energy from the *A* ion is ne-