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Electronic structure of Nb_xMo_{100-x} solid solutions

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Nb_xMo_{100-x} solid solutions ($0 \leq x \leq 100$) have been studied by means of photoelectron spectroscopy in order to obtain direct information concerning the electronic density of states of the alloy. Detailed knowledge of the density of states is relevant to the discussion of electronic properties such as the superconducting transition temperature. Changes observed in the valence-band spectra as a function of systematic changes in x follow a very simple law proposed in the early days of solid-state physics known as the rigid-band model (RBM). The observed binding energy shifts of the "rigid" valence band on alloying agree fairly well with predictions based on modern band-structure calculations for the pure components, verifying that this simple model can be used even quantitatively as has been assumed in the past. The dependence of the superconducting transition temperature on the concentration can be very well understood on the basis of this RBM description of the electronic structure.

I. INTRODUCTION

Since the discovery of superconductivity much work has been carried out to understand what parameters influence the superconducting transition temperature T_c. Bardeen, Cooper, and Schrieffer[1] gave the first expression of T_c in which the density of states at the Fermi level, $N(E_F)$, beside others, like the Debye frequency or the electron-phonon coupling constant plays an important role. This model could be improved by McMillan[2] to apply also for transition-metal– (TM-) based strong coupled superconductors, confirming the influence of $N(E_F)$ on the superconducting properties. Studying these properties in ordered as well as disordered (amorphous) TM-TM alloys, Collver and Hammond[3] emphasized the importance of the mean electron-to-atom ratio, e/a, controlling T_c as an *atomiclike* parameter in both phases. More recently the different behavior of T_c in the ordered and disordered states has been suggested by Moruzzi *et al.*[4,5] to be mainly due to a significant difference in the electronic structure. As the different authors do not agree on the parameters controlling T_c, a more elaborate picture of the band structure of TM alloys is required to investigate properly the interplay of $N(E_F)$ with T_c. The choice of studying Nb-Mo alloys is motivated firstly by the large difference of the T_c values in the crystalline and amorphous phases and secondly by the complete miscibility of the components, allowing investigations over the entire concentration range. In this work we report on photoemission experiments performed on topologically ordered Nb-Mo solid solutions. Results from the amorphous state will be published elsewhere.

In order to elaborate the understanding of the valence-band structure of an alloy system the experimental data need to be compared with theoretical predictions. Based on the development of very powerful methods during the last decade, an adequate modeling of the electronic (and atomic) structure even for very complicated systems, such as disordered alloys containing, e.g., two transition metals,[6,7] seems now to be available. This recent progress constitutes a solid base to explain, e.g., the transport[8] or the magnetic[6] properties of various systems.

The underlying concept, i.e., the prediction of physical properties on the base of band-structure calculations, was initiated originally by the work of Mott who formulated the first band-structure model for alloys using first-order perturbation theory.[9] Motts idea was to assume that the energy surfaces in k space and the density of states of the solvent metal remain unchanged on alloying. The only effect of the addition of the solute metal is to transfer part of its charge to the solvent, leading to a swelling or shrinking of the Fermi surface. This model succeeded in accounting for the magnetic properties, the transport properties,[9] as well as the structural[10] properties of some alloys. However, the validity of this simple band-structure model has been shown to be rather limited both by experiments[11,12] and by theory.[13,14] Whereas the rigid-band model (RBM) has been expected to be accurate for nearly free electron systems,[13] its applicability remained questionable for concentrated solid solutions where the solute strongly perturbs the electronic structure of the solvent, leading to a breakdown of first-order perturbation theory.[14] Although many extensions of the model[11,14–16] have been developed to better account for the distortion of the energy band on alloying, the validity range of the RBM has been reduced further.[17,18] On the basis of experimental results,[2,19,20] the Nb-Mo system is one of the few good candidates with, e.g., CrV or TaW remaining to which the RBM may apply. Support is also provided by several theoretical works revealing a very similar valence-band structure for the pure elements.[21–23] However, even for Nb-Mo alloys, arguments against the validity of the RBM have been given.[24,25]

In order to elucidate the relevance of the RBM, which is still widely used in the literature,[26–32] photoelectron spectroscopic measurements have been performed on different Nb_xMo_{100-x} solid solutions. It will be shown that this model, in combination with band-structure cal-

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culations for the pure components,[33] provides an adequate basis for the interpretation of the superconducting transition temperature within the McMillan model.

II. EXPERIMENT

bcc Nb_xMo_{100-x} solid solutions ($x = 12, 25, 40, 50, 75$) were prepared by arc melting the two components in an Ar atmosphere. The purity of the materials was 99.97% for Mo and 99.99% for Nb. The measurements were carried out at room temperature on a Fisons ESCALAB 210 spectrometer operating at a base pressure below 3×10^{-10} mbar. A sample surface cleaning process by Ar^+ ion etching at 3.5 keV was first performed for 20–40 min. Additional short cleaning by ion bombardment has been applied in the course of photoelectron spectroscopy after each energy sweep.

Photoelectrons were excited by means of either UV light from a conventional discharge lamp [ultraviolet photoemission spectroscopy (UPS) He I: 21.2 eV, UPS He II: 40.8 eV] or monochromatized x rays [monochromated x-ray photoelectron spectroscopy (MXPS) Al $K\alpha$: 1486.6 eV]. The total energy resolution (full width at half maximum) was 0.07 eV for the He I, 0.14 eV for the He II, and 0.3 eV for the MXPS measurements, respectively.

UPS has been used to investigate the valence-band structure of the samples, MXPS to excite valence states as well as core levels. The surface composition of the alloys evaluated by analyzing the core-level intensities was found to correspond to the concentrations defined at the preparation within an experimental error of 4%, indicating that preferential sputtering effects during the cleaning procedure can be neglected. No carbon impurities were discernible, while the surface oxygen content was evaluated to lie below 2%.

III. RESULTS AND DISCUSSION

Valence-band spectra measured at an excitation energy of 21.2 eV on Nb_xMo_{100-x} solid solutions are shown in Fig. 1 together with the total density of states (DOS) curves as calculated by Moruzzi[33] for the pure elements in the bcc structure (dashed lines). The angular momentum decomposed DOS calculations show that the valence bands of Nb and Mo mainly consist of d states. The valence band is split into two sub-bands (bonding, antibonding) separated by a pseudogap, which is typical for the TM in the body-centered cubic structure.[4] Three major peaks (labeled A, B, and C) are visible for both elements reflecting the bonding part of the d band. In the case of Nb these peaks are located at binding energies of 2.5, 1.4, and 0.2 eV (Ref. 33), respectively. Obviously the theoretical band shape is very similar for Nb and Mo, the only difference being the position of the Fermi level E_F as indicated by arrows. E_F lies at the edge of the bonding part of the valence band for Nb, while for Mo, containing one more electron per atom, it is located on the other side of the pseudogap, which separates the bonding from the antibonding states.

The major peaks A, B, and C, which can be identified in all experimental results, have been aligned in order to observe the development of the band shape upon alloying. Starting with the spectrum of pure Nb where all characteristic features are present as predicted by theory, the addition of an increasing amount of Mo leads to a systematic shift of the Fermi edge across the pseudogap, i.e., to a continuous filling of empty electron states. At the same time the shape as well as the relative positions of the major structures A, B, and C remain nearly constant. This supports the "rigid" behavior of the valence band upon alloying over the *whole* range of composition. This rigid-band behavior, confirmed by recent local spin-density band structure calculations of Hafner and coworkers,[34] can be seen in Fig. 2 in more detail, where the energy range of the pseudogap has been plotted on an enlarged scale. Clearly, all the photoemission spectra

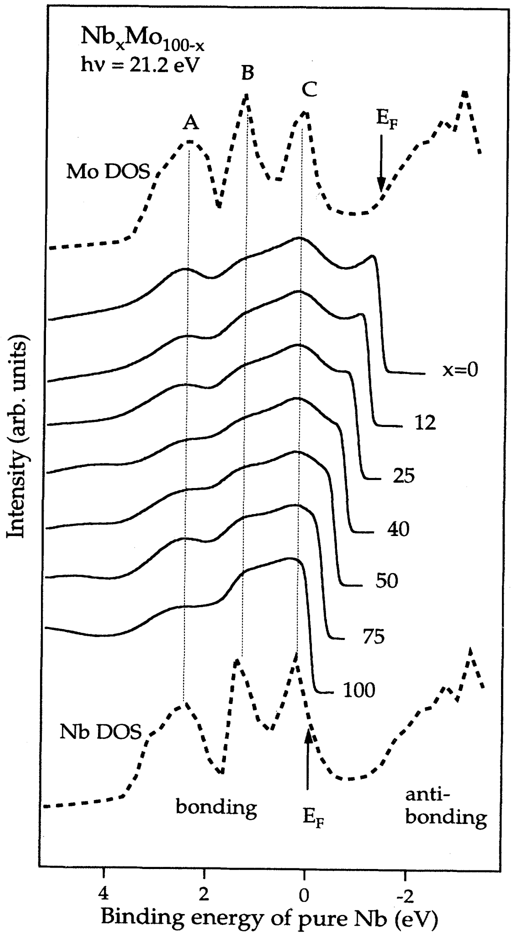

FIG. 1. Valence-band structure of Nb_xMo_{100-x} solid solutions as a function of x. Full lines: photoelectron spectra measured at an excitation energy of 21.2 eV. They have been normalized to the same height and have been shifted on the energy scale to line up with the major structures. No other corrections have been applied. Dashed lines: theoretical DOS for Mo and Nb (Ref. 33).

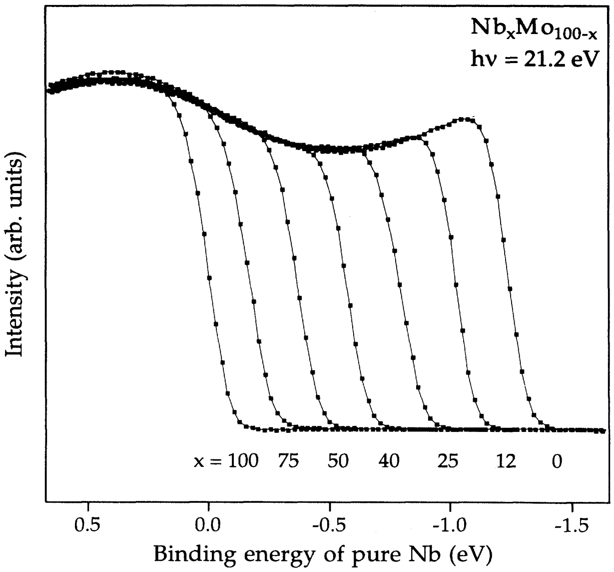

FIG. 2. Valence-band spectra from Fig. 1: region near E_F is on an enlarged scale.

presented resemble the same principal band shape, the only effect of alloying being a different position of the Fermi edge, which is smeared out by the combined effects of the resolution function of the spectrometer and the Fermi distribution function. These observations are different from those of Indlekofer *et al.*[35] in the V-Mo system, who found a rigid-band-like behavior only on the Mo-rich side of the alloys.

Because photoemission results usually have to be interpreted as a sum of partial densities of states weighted by the corresponding photoionization cross sections, significant differences in the excitation of Nb-derived and Mo-derived states cannot be excluded for the results presented in Figs. 1 and 2. Therefore valence-band spectra have also been taken at higher photon energies in order to study the influence of cross-section effects. In Figs. 3 and 4 valence-band results are summarized for excitation energies of 40.8 eV (Fig. 3) and 1486.6 eV (Fig. 4). In both sets of data all the significant features of the valence-band spectra, i.e., peaks *A*, *B*, *C*, and the pseudogap can be seen, demonstrating the same systematic trends found in Fig. 1. Other effects such as the optical direct transition giving rise to distortions in this experimental picture of the DOS can be ruled out in this case in view of the good consistency obtained for all these excitation energies. These results corroborate the validity of the RBM for ordered Nb-Mo solid solutions, at least in a qualitative manner.

As can be seen in Figs. 1, 3, and 4, discrepancies exist between the theoretical and experimental band shape for the pure elements concerning the relative intensities of the major peaks. These discrepancies are partly due to matrix element effects related to the transition of the photoelectrons, to a smearing out of sharp structures due to lifetime effects of the photoionized hole states and to a smearing out by the resolution function of the electron energy analyzer. Therefore, at first sight, it seems to be impossible to proceed to a more rigorous, i.e., quantitative, test of the RBM. However, the observed shift of the Fermi level upon alloying that we observed suggested that a quantitative description of the band filling when passing from pure Nb to pure Mo might be possible. Using, e.g., Mo as a reference, its theoretical band shape can be used to estimate the rigid shift of E_F by integrating the DOS curve to such a value that corresponds to the mean number of electrons per atom for a given alloy composition. The expected energy shifts are presented in Fig. 5 together with experimentally determined values extracted from Figs. 1, 3, and 4 for the different photon energies. Apparently, both sets of data agree fairly well, giving fur-

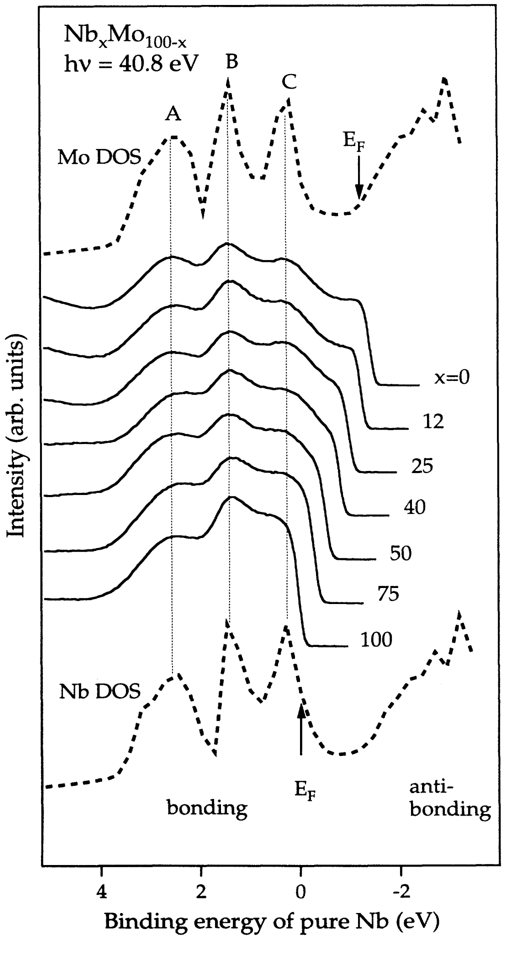

FIG. 3. Valence-band structure of Nb_xMo_{100-x} solid solutions as a function of x. Full lines: Photoelectron spectra measured at an excitation energy of 40.8 eV. They have been normalized to the same height and have been shifted on the energy scale to line up with the major structures. No other corrections have been applied. Dashed lines: theoretical DOS for Mo and Nb (Ref. 33).

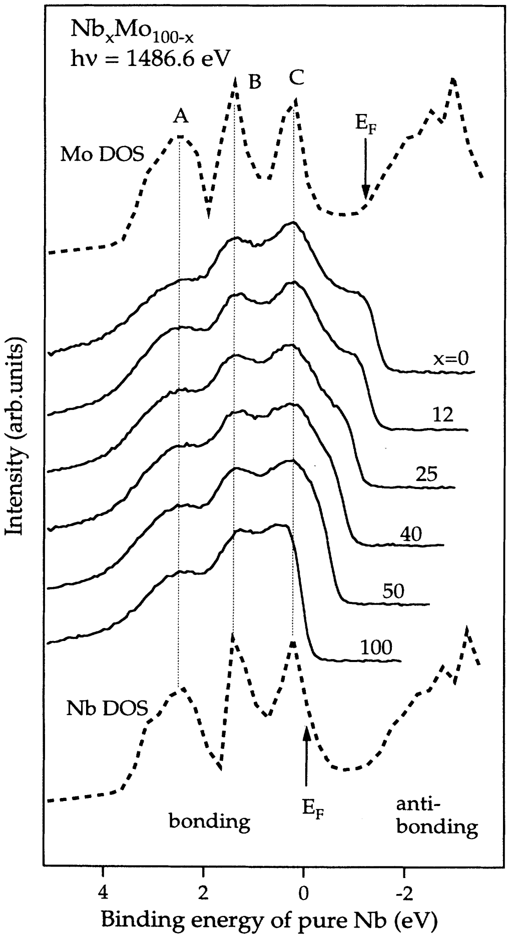

FIG. 4. Valence-band structure of Nb_xMo_{100-x} as a function of x. Full lines: photoelectron spectra measured at an excitation energy of 1486.6 eV. The spectra have been normalized to the same height and have been shifted on the energy scale to line up the major structures of the band. A nonlinear background has been substracted. Dashed lines: theoretical DOS for Mo and Nb (Ref. 33).

ther support to the validity of the simplest band-structure model for Nb-Mo solid solutions.

Once it has been established that the RBM describes the evolution of the valence-band structure of Nb-Mo solid solutions, it may then be used to analyze their physical properties. For this purpose $N(E_F)$ values as deduced within the RBM from the theoretical DOS have been plotted in Fig. 6 for different alloy concentrations (full symbols) representing the filling of the pseudogap upon alloying. These data can be compared to experimental values (open symbols), which have been extracted from T_c data and specific-heat measurements. Obviously both sets of data agree fairly well, emphasizing the strong interplay between the electronic structure and the superconducting properties for such strong coupled superconductors. In a separate paper we will discuss the enhanced T_c values measured by Collver and Hammond[3] in the

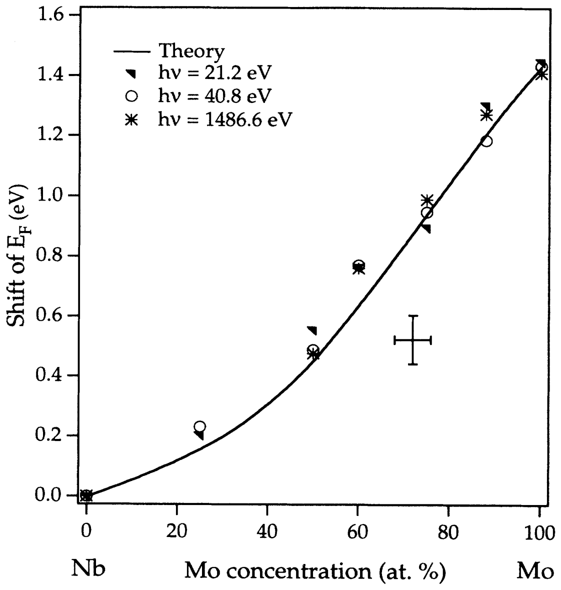

FIG. 5. Shift of E_F along the rigid valence band, as a function of the Mo concentration. Line: deduced from Moruzzi band-structure calculations of Mo (Ref. 33) within the RBM picture. Full triangle: experimental He I shifts of E_F from Fig. 1. Open circle: experimental He II shifts of E_F from Fig. 3. Stars: experimental MXPS shifts of E_F from Fig. 4.

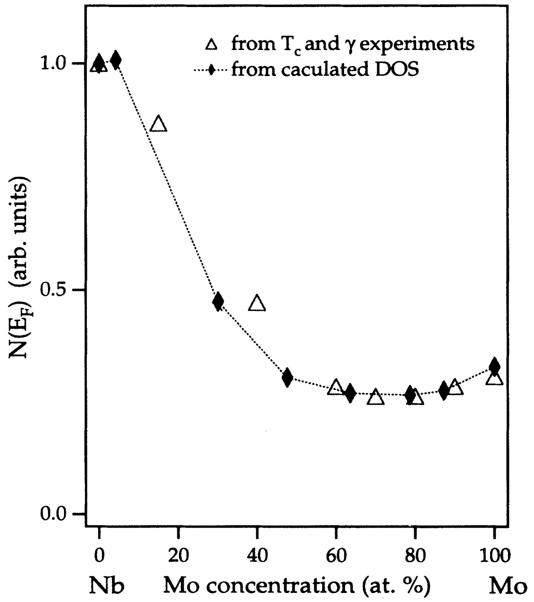

FIG. 6. Evolution of $N(E_F)$ as a function of the Mo concentration. The curves have been normalized for pure Nb. Full squares: $N(E_F)$ derived from the theoretical Mo DOS (Ref. 33). Triangles: from T_c and γ measurements (Ref. 2).

amorphous phase as compared to their crystalline counterparts in terms of the DOS near the Fermi level.

IV. CONCLUSIONS

Using photoelectron spectroscopy Nb-Mo solid solutions are found to be very well described within the original version of the RBM. For all alloy compositions a rigid behavior of the band structure is observed, the only difference being the location of the Fermi level. These measurements confirm the application of this model as an important input in the discussion of the superconducting properties underlining the close connection between the superconducting transition temperature T_c and the electronic density of states at the Fermi level in this alloy system.

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