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dicted cancelation. During the pulse the crystal temperature rises by one or two degrees which may explain the flatness of the minimum but not the observed absolute magnitude of the signal. Thermalization of the absorbed CO₂-laser radiation might get sufficiently slow at these temperatures to influence the coupling parameter by a nonequilibrium phonon distribution. We do not believe that the investigated normal-quality crystal allows for a well-developed second-sound mode but deviations from the diffusive law might also exist. The answer to these interesting questions will require considerably more work which is beyond the scope of this report. We are planning to extend the forced-Rayleigh-scattering technique to rf-modulated pump radiation in order to investigate the low-temperature Rayleigh peak in more detail.

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X-Ray Photoemission Study of Some Light Rare-Earth Metals

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We present an x-ray photoemission spectroscopy study of the rare earths La, Ce, Pr, and Nd. We show that the spectra of these metals in the vicinity of the Fermi energy account for the 4f levels as well as for the valence states. The energy location of the 4f electrons is in fairly good agreement with an existing computation performed in the framework of the renormalized-atom method.

The energy position of the outer electronic levels in rare-earth metals has already been the subject of various photoemission studies.¹⁻⁷ Conventional uv light ($\hbar \omega \leq 11 \text{ eV}$) is not very suitable for exciting 4*f* electrons because of the small matrix elements for the excitation of the *d* states of the continuous spectrum (ϵd) and because of the poor overlap of the 4*f* wave functions with the ϵg wave functions which are hindered by centrifugal repulsion from penetrating deep into the atom cores at low kinetic energies. uv-photoemission spectra give information about valence states but hardly reveal the existence of 4*f* electrons. In contrast, it has been thought until now that soft x-rays would predominantly excite the 4f electrons. The spectra of rareearth metals obtained by x-ray photoemission spectroscopy (XPS) were interpreted exclusively in terms of 4f levels and a satisfactory agreement was found with the general predicted features of these states.¹⁻³ For Sm and Nd, however, the appearance of a peak near the Fermi level does not correspond at all to the expected behavior of the 4f electrons as a function of the atomic number. The origin of this peak is not well understood. For example, excited final states are likely to be observed in incomplete shells but they always appear in the spectra at higher binding energies than the ground state. The possible location of the 4f ground state just VOLUME 31, NUMBER 1

below the Fermi energy in Sm and Nd seems incompatible with the relatively high binding energy of the single peak corresponding to the halffilled shell of Gd.³ A 4f ground state near $E_{\rm F}$ is expected in divalent metals where the 4f electrons are weakly bound as a result of the increased Coulomb repulsion. However it is today well established that, except for Eu and Yb, all rare-earth metals are trivalent. The occurrence of oxide peaks or strong plasmon losses can also be ruled out and any simple explanation of the Sm and Nd spectra based on 4f states only seems highly unlikely. Furthermore, in contrast to Sm and Nd, only one peak has been reported for Pr.⁸ This intriguing situation has incited us to initiate a new XPS study of these metals.⁹

In this communication we report on the four rare earths La, Ce, Pr, and Nd. These metals with a low number of f electrons have been selected because of their particularly simple spectra. All the other rare earths, except for Eu and Gd, show multiple final states which will require a rather elaborate interpretation. The samples have been prepared by fast evaporation in situ from pure materials (99.9%). Small amounts of the metals were put in tungsten baskets and carefully outgassed until the evaporation could take place in a vacuum better than 2×10^{-9} Torr. The base pressure of the system was very low (2 \times 10⁻¹¹ Torr) but still not good enough to prevent a very weak O 1s signal from growing slowly during the measurements. No change in the spectra of the valence-band region could be correlated with the increase of the oxygen signal, insuring that our results are characteristic of the metals. The measurements have been performed in our special ES 100 photoelectron spectrometer manufactured by AEI Scientific Apparatus. The $K\alpha_{1,2}$ emission line of Mg was used and the total instrumental resolution was slightly better than 1.0 eV.

Figure 1 reproduces the XPS spectra of the four metals in a range of 10 eV below the Fermi energy. The position of the Fermi level has been determined within an accuracy of ± 0.1 eV by comparison with the valence-band spectrum of Pd.¹⁰ The relative intensities of the different spectra are arbitrary. The structures arising at binding energies higher than 5 eV in the La spectrum correspond to 5*p* electrons excited by the x-ray satellite $K\alpha_{3,4}$. The other spectra have been cut off before the onset of these structures. La has not been studied previously by photoemission but the densities of states of the neighboring



FIG. 1. Comparison of the XPS spectra of the first rare-earth metals.

transition metals (Y, Zr, Hf) show common features.⁵ They are relatively high at the Fermi energy and exhibit some structure as they decrease toward higher binding energies. The total width of the bands is of the order of 5 eV. This general trend seems to hold for the valence bands of the whole series or rare-earth metals.^{4-6,11} With the resolution of XPS, the fine structure will not be resolved and the smooth decrease toward the bottom of the bands will be swamped in the rising background of scattered electrons. The first peak just below the Fermi level in the spectra of La, Pr, and Nd is attributed to the d states of the valence band, which contribute mostly to the high density of states in the vicinity of the Fermi energy. The techniques used to compute the s-d bands in the rare-earth metals are not suitable to detemine the position of the occupied 4f levels. These localized electrons, which have large intra-atomic exchange and correlation energies, cannot be treated in the same manner as valence states. The renormalized-atom scheme has been recently applied to calculate the position of the 4f levels in rare-earth metals.¹² The one-electron renormalized-atom approach yields energies which are obviously too large when comVOLUME 31, NUMBER 1

pared to experimental values. More pertinent in connection with photoemission are the placements of the 4f states obtained by the multielectron method taking into account relaxation effects when one electron is removed. The multielectron predictions for the 4f shells are approximately¹³ 4.1 and 5.1 eV for Pr and Nd, respectively. In addition to the valence-band structures which remain stationary, the XPS spectra show 4f peaks at 3.4 eV for Pr and 4.8 eV for Nd, in fairly good agreement with the computed values. The spectrum of Ce does not show clearly the separation between d and f states. The flat shape of the broad peak indicates however that two unresolved structures are present. In connection with this XPS spectrum, it is useful to consider the energy distribution curve of photoelectrons excited by uv light.¹⁴ The curve recorded for a clean Ce surface shows the typical feature of an s-d band, while no evidence of a 4f level can be observed. It seems reasonable to assume that our spectrum is formed by a valence band rather similar to that of La and by a 4f peak at higher binding energies. An approximate deconvolution yields an energy of 1.8 eV for the 4f level, in good agreement with the value of 2.0 eV predicted by the multielectron calculation. Our interpretation of the four spectra is strengthened by the observation of the relative intensity increase from Ce to Nd of the 4f signal compared to the valence-band signal. Unfortunately the separation of the two structures and the subtraction of the background are too arbitrary for a precise intensity determination. The spectra have been tentatively normalized to the intensity of the 5p core levels. The valence-band intensities are then contained in a range of $\pm 20\%$ around a mean value while

the 4f intensities are nearly proportional to the expected number of these electrons, i.e. 1 to 3 from Ce to Nd. It is clear from these results that the probability per electron of excitation by soft x rays is of the same order of magnitude for d and f symmetry. Thus, the spectra presented in this study can be considered as rather reliable pictures of the outer levels of light rare-earth metals.

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Harmonic-Phonon Generation by Shear Waves in V₃Si

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The generation of second-harmonic ultrasound (5 to 10 MHz) with an estimated conversion efficiency $\gtrsim 20\%$ has been observed for the soft shear mode in V₃Si below 77°K. The harmonic generation is a manifestation of the unusually large shear anharmonicity for this unstable compound; however, static symmetry arguments forbid the generation of an even-ordered harmonic for a high-symmetry shear wave in a cubic crystal. Several possible sources of symmetry reduction are discussed.

The A-15 structure compounds have provided the first and the most detailed examples of the interrelation of structural instability and hightemperature superconductivity.¹⁻⁴ In addition to the soft modes and structural transformations exhibited by these compounds, a complicating but