

quite small, at least in the Silverstein approximation. The principal contribution to the shift comes from  $\Delta_P$  and  $\Delta_L$ , with the change in  $\chi^0$  caused by the change in density somewhat smaller. The unfavorable aspect of the susceptibility shift is that it is quite small. Again excepting Pb, the theory predicts the correct sign for the shift, and for some metals gives a fair account of its magnitude. It should be emphasized again that the error in the experimental results is quite large.

The qualitative agreement with experiment for the alkalis and the trivalent metals indicates that the basic physical picture considered here is an adequate one for these materials. The metal is represented by a distribution of point ions, immersed in a sea of interacting electrons. Perhaps the calculated susceptibilities could be brought closer to the experiments by a better treatment of the electron-electron interaction which both correlates the spins and screens the ion potential.

The theory does not seem to work for the divalent metals. The experimental susceptibility above the melting point is much smaller than the free-electron value

and strongly temperature-dependent.<sup>19</sup> There is evidence from the Knight shift in Cd that  $\chi_P$  takes the free-electron value and is temperature-independent.<sup>20</sup> Some new physics, probably involving the  $d$  electrons, will be needed to understand the susceptibility of these liquids.

### VIII. CONCLUSIONS

The objective of the investigation has been to calculate the effect of the ion potentials on the susceptibility of liquid metals in terms of the liquid-structure factor and the ion pseudopotential. This correction turns out to be small and can be of either sign. When correlation of the electron spins is taken into account, a larger effect than the ion-potential corrections, the calculated susceptibilities are in rough agreement with experiment for some simple metals. Estimates of the shift in susceptibility on melting also are roughly confirmed by experiment.

<sup>19</sup> A. Menth (private communication.)

<sup>20</sup> R. V. Kasowski and L. M. Falicov, Phys. Rev. Letters **22**, 1001 (1969).

## Energy Bands for fcc Lanthanum and Praseodymium†

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We have calculated the energy bands of lanthanum and praseodymium in the face-centered-cubic structure using the relativistic augmented-plane-wave method. Calculations for the density of states, the magnetic susceptibility, and the Fermi surface are also performed, and the results are correlated with some of the electronic and magnetic properties of these metals.

**L**IGHT rare earths La ( $Z=57$ ), Pr ( $Z=59$ ), and Nd ( $Z=60$ ) can be stabilized in two crystal structures, namely, double hexagonal close-packed (dhcp) and face-centered cubic (fcc).<sup>1,2</sup> Both phases of La are superconducting at sufficiently low temperatures with slightly different superconducting and normal state parameters.<sup>1</sup> Pr and Nd in the dhcp phase order antiferromagnetically at low temperatures, while in the fcc phase, they order ferromagnetically.<sup>2,3</sup> In this paper, we report results of the band calculation of fcc La and Pr and compare them with similar calculations for these metals in the dhcp phase.<sup>4</sup> It will be shown that the differences in superconducting or magnetic proper-

ties between the two phases can be understood from the differences in their band structures.

The relativistic augmented-plane-wave (RAPW) method is used for the band calculation.<sup>5,6</sup> The muffin-tin potential is constructed in the standard way from the atomic electron charge density.<sup>7</sup> The Slater  $\rho^{1/3}$  exchange energy is assumed. The electronic configuration used for La is  $5d^16s^2$  and is  $5d^06s^2$  for Pr. The lattice parameters are  $a=10.011$  a.u.<sup>8</sup> (5.296 Å) for La and 9.804<sup>2</sup> a.u. (5.186 Å) for Pr. The lattice parameter for fcc Nd has not been determined. The radius of the muffin-tin potential is chosen as 3.158 a.u. The relativistic analog of the logarithmic derivative of the wave function is found to be divergent in the energy

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<sup>1</sup> D. L. Johnson and D. K. Kinnemore, Phys. Rev. **158**, 376 (1967).

<sup>2</sup> E. Bucher, C. W. Chu, J. P. Maita, K. Andres, A. S. Cooper, E. Buehler, and K. Nassau, Phys. Letters **22**, 1260 (1969).

<sup>3</sup> W. C. Koehler, J. Appl. Phys. **36**, 1078 (1965).

<sup>4</sup> G. S. Fleming, S. H. Liu, and T. L. Loucks, Phys. Rev. Letters **21**, 1524 (1968).

<sup>5</sup> T. L. Loucks, Phys. Rev. **139**, A231 (1965).

<sup>6</sup> T. L. Loucks, *Augmented Plane Wave Method* (W. A. Benjamin, Inc., New York, 1967).

<sup>7</sup> D. Liberman, J. T. Waber, and D. T. Cromer, Phys. Rev. **137**, A27 (1965).

<sup>8</sup> W. B. Pearson, *Handbook of Lattice Spacings and Structures for Metals and Alloys* (Pergamon Press, Inc., New York, 1958).

FIG. 1. Energy bands for La plotted in the high-symmetry directions.

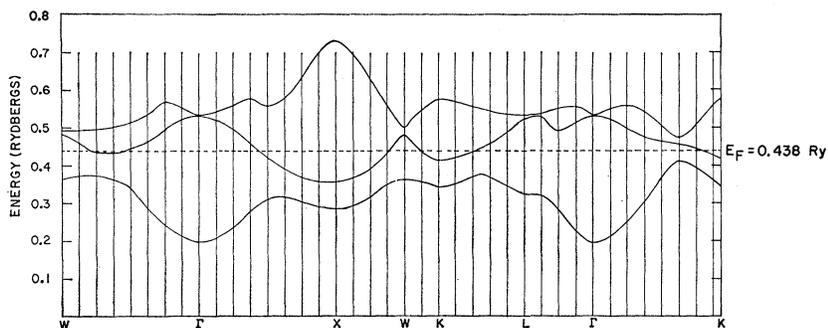
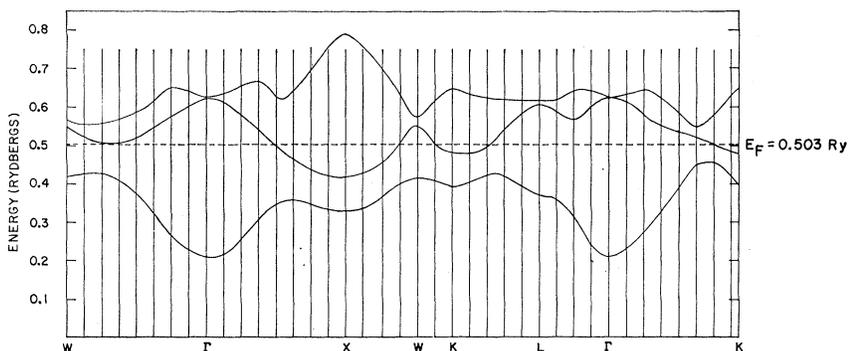


FIG. 2. Energy bands for Pr plotted in the high-symmetry directions.



range of interest for  $\kappa=3$  and  $-4$ . The singularities are removed by straight-line interpolation as done previously for rare earths and thorium.<sup>9,10</sup> A set of 40 plane waves (recips) is needed in the trial wave function for La in order that the eigenvalues converge to within 0.001 Ry, while for Pr a set of 35 recips is found to be sufficient. The same set of recips is used to cal-

culate the energy eigenvalues at 89 points uniformly distributed in a  $1/48$  sector of the Brillouin zone. The corners of the sector are the high-symmetry points  $\Gamma$ , X, W, K, U, and L whose coordinates are given in Table I. For the determination of the density of states and Fermi surface, we use the spline-interpolation scheme to cover the Brillouin zone with a finer mesh of 256 000 points in the zone.

The energy bands for La and Pr in the high-symmetry directions are plotted in Figs. 1 and 2, respectively.

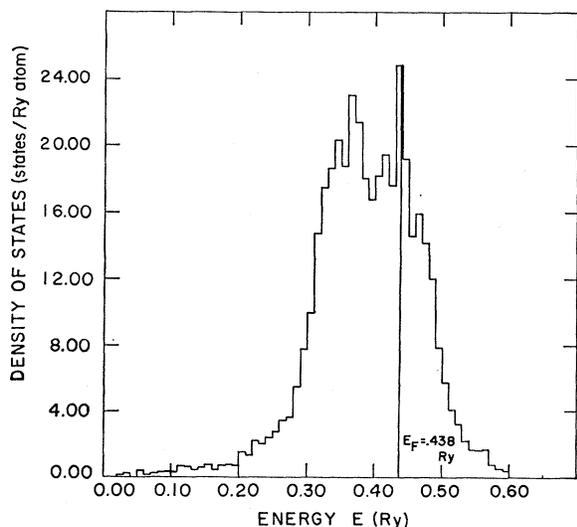


FIG. 3. Density-of-states curve for La.

<sup>9</sup> S. C. Keeton and T. L. Loucks, Phys. Rev. **168**, 672 (1968).

<sup>10</sup> R. P. Gupta and T. L. Loucks, Phys. Rev. Letters **22**, 458 (1969).

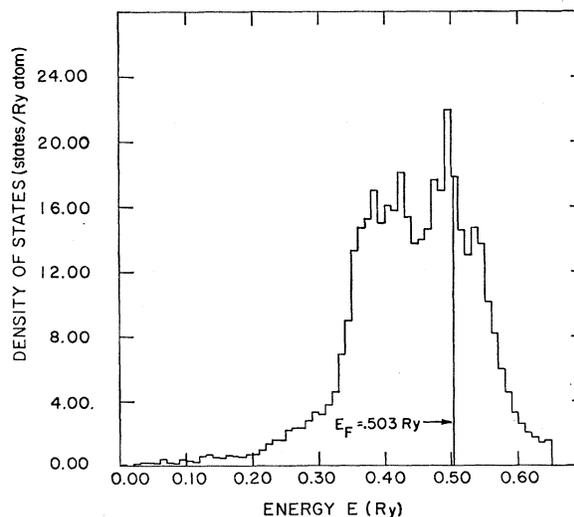


FIG. 4. Density-of-states curve for Pr.

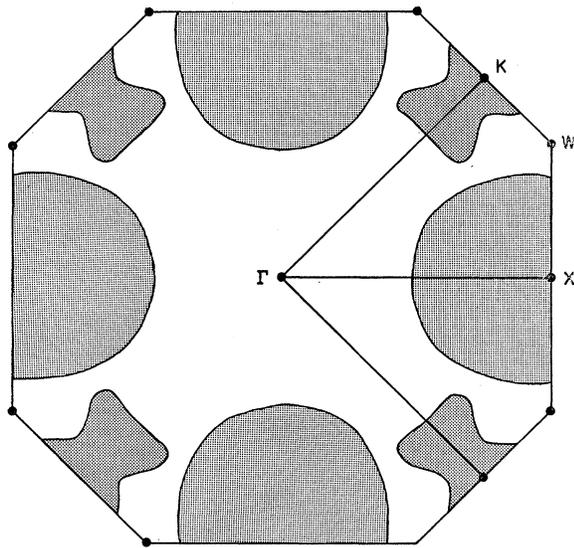


FIG. 5. Cross section of Pr Fermi surface in (100) plane.

From these bands, the density of states at the Fermi energy are found to be 24.8 states/Ry atom for La and 17.8 for Pr (Figs. 3 and 4). The experimental value of  $N(\epsilon_F)$  for fcc La is 33.6 before the electron-phonon mass enhancement correction is made.<sup>11</sup> After the correction is made according to the McMillan formula,<sup>11</sup> the experimental value reduces to 17.3.<sup>12</sup> Our result is in the correct range, but it seems to indicate that the mass enhancement factor is overestimated. Similar calculation for dhcp La gives  $N(\epsilon_F)=19.4$  states/Ry atom while the experimental value is 27.2 before the

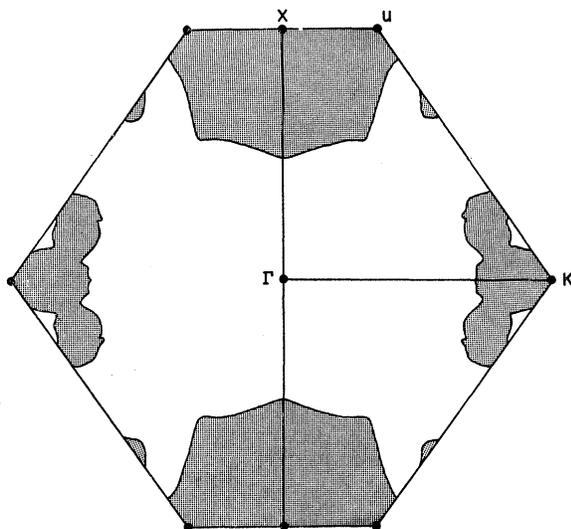


FIG. 6. Cross section of Pr Fermi surface in (110) plane.

<sup>11</sup> W. L. McMillan, Phys. Rev. 167, 331 (1968).<sup>12</sup> D. K. Finnemore (private communication).

TABLE I. Coordinates of high-symmetry points.

	$k_x$	$k_y$	$k_z$
$\Gamma$	0	0	0
$X$	8	0	0
$W$	8	4	0
$K$	6	6	0
$U$	8	2	2
$L$	4	4	4

mass enhancement correction and 14.1 after the correction. The ratio of the densities of states at the Fermi level for dhcp and fcc La agrees very well with that of the experimental values, with or without mass enhancement correction. There has been no measurement of the density of states at the Fermi energy for fcc Pr.

The Fermi surfaces of fcc La and Pr are very similar to that of actinium.<sup>13</sup> They are multiply connected surfaces and are very difficult to depict graphically. We choose to illustrate the Fermi surface of Pr in terms of its cross sections in the (100), (110), and (111) planes as shown in Figs. 5-7. In these figures, the occupied regions are shaded. The Fermi surface of La has an additional electron pocket between  $\Gamma$  and  $W$ . The energy band which defines this pocket is very flat, and, consequently,  $N(\epsilon_F)$  for La is significantly larger than for Pr.

In a magnetic metal, where the local moments are coupled by the indirect exchange mechanism via the conduction electrons, there is a strong dependence of the magnetic ordering on the electronic energy bands and the Fermi-surface geometry.<sup>9,14</sup> The relationship between the energy bands and the magnetic ordering has been explored by the generalized susceptibility

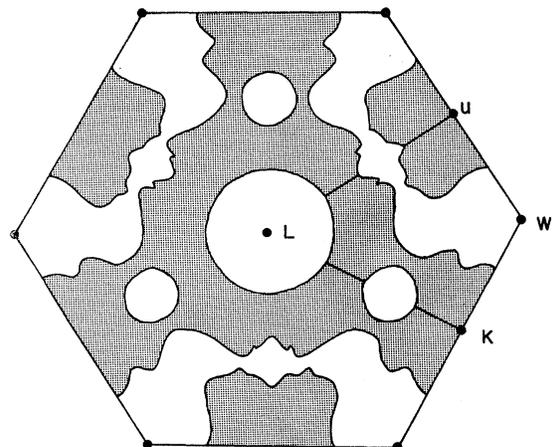


FIG. 7. Cross section of Pr Fermi surface in (111) plane.

<sup>13</sup> R. P. Gupta (private communication).<sup>14</sup> W. M. Lomer, Proc. Phys. Soc. (London) 80, 489 (1962).

FIG. 8. Generalized susceptibility of Pr(dhcp) from  $\Gamma \rightarrow M$ .

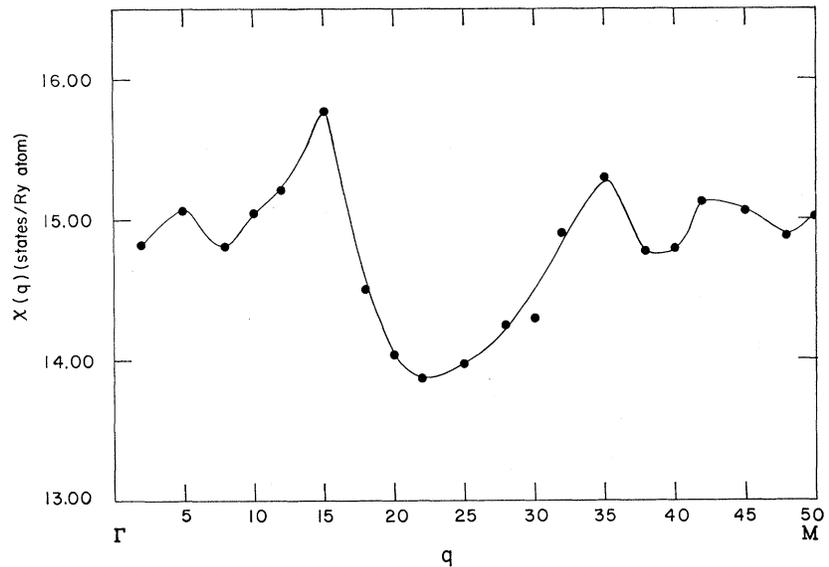
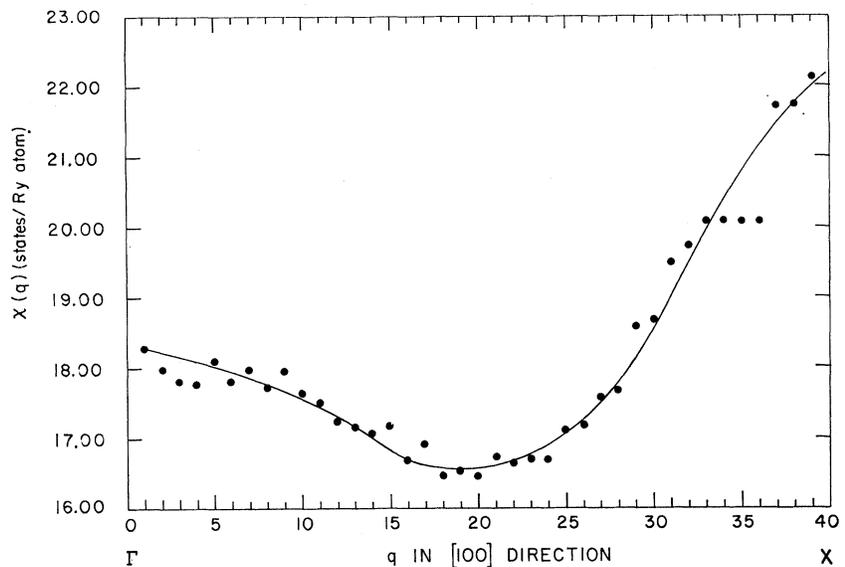


FIG. 9. Generalized susceptibility of Pr(fcc) from  $\Gamma \rightarrow X$ .



$\chi(q)$  calculation.<sup>15-18</sup> The wave vector for the stable periodic moment structure corresponds to the position of the peak of  $\chi(q)$ . In Figs. 8 and 9, we show the  $\chi(q)$  curves for dhcp Pr for  $q$  along  $\Gamma M$  direction and for fcc Pr for  $q$  along  $\Gamma X$  direction. These curves are computed in the same manner as described in Ref. 15. For dhcp Pr, there is a peak at  $q=0.15b_1$ , while, for fcc Pr, there

are two peaks located at  $\Gamma$  and  $X$ . The peak at  $X$  corresponds to a sizable wave vector, so it may be strongly suppressed by a wave-vector-dependent matrix element.<sup>16,19</sup> If this is the case, then the peak at  $\Gamma$  will dominate, and the ordering of the moments in the fcc Pr will be ferromagnetic. This may explain the difference in magnetic ordering properties of the two phases of Pr and Nd.

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<sup>15</sup> W. E. Evenson and S. H. Liu, Phys. Rev. Letters 21, 432 (1968).

<sup>16</sup> W. E. Evenson and S. H. Liu, Phys. Rev. 178, 783 (1969).

<sup>17</sup> G. S. Fleming, S. H. Liu, and T. L. Loucks, J. Appl. Phys. 40, 1285 (1969).

<sup>18</sup> G. S. Fleming, W. E. Evenson, and S. H. Liu, Phys. Rev. 178, 930 (1969).

<sup>19</sup> R. E. Watson and A. J. Freeman, Phys. Rev. 152, 566 (1966).