[10]E. L. Zorina, Opt. Spectrosk. 27, 320 (1969) [Opt. Spectrosc. (USSR) 27, 168 (1969)], observed an absorption tail in vitreous As_2S_3 at a much higher absorption level, but this is very probably due to a higher content of impurities in her samples. She interprets the absorption tail as due to indirect phonon-assisted transitions. It is not possible to explain our curves this way because the required phonon energies would have to be much too high and the temperature dependence of the slopes for our curves cannot be reconciled with this interpretation.

[11]J. Tauc, R. Grigorovici, and A. Vancu, Phys. Status Solidi 15, 627 (1966).

[12]The hydrogenic model [D. M. Eagles, J. Phys. Chem. Solids 16, 76 (1960)] and the Koster-Slater model [J. C. Slater, in Handbuch der Physik, edited by S. Flügge (Springer, Berlin, 1956), Vol. 19, Pt. I, p. 67] give essentially the same formula; the changes of the conduction-band states by the impurity potential are neglected in all these approaches.

CRYSTAL FIELDS IN RARE-EARTH METALLIC COMPOUNDS

K. C. Turberfield* and L. Passell

Brookhaven National Laboratory,† Upton, New York 11973

and

R. J. Birgeneau‡ and E. Bucher

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 21 July 1970)

Neutron crystal-field spectroscopy has been carried out in a series of praseodymium monochalcogenides and monopnictides; the results illustrate the power of inelastic neutron scattering techniques in such problems. It is found that all of the crystal-field levels in all compounds studied can be quantitatively accounted for by use of a simple point-charge model.

The magnetic properties of rare-earth metals and metallic compounds are profoundly influenced by the crystal field.[1] However, because of the difficulty of doing unambiguous experiments there is at the present time only very limited experimental information available on the crystal field itself.[2] In addition, most of the existing theories for its microscopic origins are speculative in nature.[3] This is in sharp contrast to the situation in insulators, where the energy-level schemes of rare-earth ions over many J multiplets are accurately known in a wide variety of materials.[4] Furthermore, it has proven possible to calculate these splittings from first principles to much better than an order of magnitude.[5] The reason for the lack of empirical information in metals is, of course, the difficulty in doing photon spectroscopy in metallic systems. However, these difficulties can be circumvented by using thermal neutrons instead of photons as the probe, and indeed, a crystal-field transition has been

observed with neutrons recently in the metal CeAs by Rainford et al.[6] In this Letter we report inelastic neutron-scattering measurements on a series of rare-earth metallic compounds. These confirm that neutrons may indeed be effectively used for rare-earth crystal-field spectroscopy in the far infrared provided only that the exchange field is somewhat smaller than the crystal field. In addition, in the materials we have studied we find that an effective point-charge model[7] is surprisingly accurate in predicting both the magnitudes and the systematics of the Stark splittings. This latter result is not understood at all.

We consider first the neutron-scattering aspects of the problem. In general, the scattering cross section for a system possessing both spin and orbital angular momentum is quite complicated. However, if we are operating within a given J multiplet and if, in addition, we limit ourselves to small momentum transfers, then the cross section for a single ion simplifies to[8]

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{1.91e^2}{2mc^2}\right)^2 \frac{k_f}{k_i} f^2(Q) \sum_{nm} \rho_n |\langle n|J_\perp|m\rangle|^2 \delta\left(\frac{E_n-E_m}{\hbar}-\omega\right), \tag{1}$$

where $|n\rangle$, $|m\rangle$ are states belonging to a given J multiplet; $J_\perp$ is the component of the total angular momentum operator perpendicular to the scattering vector $\vec{Q}$; and the remaining symbols have their usual meaning.[8] The effect of increasing the momentum transfer $|\vec{Q}|$ is to decrease the magnetic-dipole transition intensities via the form factor $f(\vec{Q})$ and also to make allowed magnetic octupole and pos-

sibly higher-order transitions.[9,10] Crystal-field transitions may be readily distinguished from phonon processes by both the spatial and thermal variation of the intensities. One-phonon peak intensities vary as Q^2, whereas crystal field peaks follow $f^2(Q)$; similarly, phonons obey Bose statistics, whereas the crystal-field levels obey Boltzmann statistics.

The experiments which we report in this note were carried out in the 1:1 praseodymium chalcogenides and pnictides. These compounds all have the rock-salt structure. In a simple picture, the chalcogenides may be thought of as essentially ionically bound compounds with the Pr in a 3+ state and the chalcogen in a 2− state and with the extra electron from the Pr^{3+} going into a conduction band which is $(5d, 6s)$-like. There are a variety of measurements which support this view.[11] The pnictides, on the other hand, are somewhat more problematic. Using valence arguments one might have expected them to be semiconductors analogous to the III-V compounds. In fact, however, most of the rare-earth pnictides exhibit quite low resistivities, typically 10^{-3} to 10^{-4} Ω cm at room temperature with positive temperature coefficients.[11] The measured carrier concentrations are one to two orders of magnitude lower than the chalcogenides. Although a proper characterization of the intrinsic properties of the rare-earth pnictides must await better materials, we may at least say that the actual materials presently available do indeed behave like metals but with densities of states significantly lower than the corresponding chalcogenides.

These sets of compounds therefore offer the possibility of doing a systematic study of crystal fields in rare-earth metallic compounds. By going down either the Va or VIa columns we may examine the effects of ionic size, and by comparing equivalent compounds in the two columns we should be able to see effects from changing the ligand charge, the covalency, and the carrier concentration.

The Pr^{3+} ion has the configuration $4f^2$ with the free-ion $^3H_4$ multiplet lying lowest. The next highest J multiplet $^3H_5$ lies at ~2150 cm^{-1} and may be effectively ignored for our purposes here. The crystal-field Hamiltonian for the O_h symmetry appropriate to the rock-salt structure may be written

$$H_{cf} = A_4\langle r^4\rangle\chi_4[O_4^{\,0}(J) + 5O_4^{\,4}(J)]$$
$$+ A_6\langle r^6\rangle\chi_6[O_6^{\,0}(J) - 21O_6^{\,4}(J)], \quad (2)$$

where the $O_n^{\,m}$ are the usual Stevens operator equivalents and the χ_n are reduced matrix elements.[7] The Hamiltonian (2) has been diagonalized for all J as a function of $A_4\langle r^4\rangle/A_6\langle r^6\rangle$ by Lea, Leask, and Wolf[12] (LLW) and the results have been conveniently tabulated by them. The Pr^{3+} $^3H_4$ manifold is found to split into four levels Γ_1, Γ_3, Γ_4, and Γ_5. For magnetic-dipole selection rules the transitions $\Gamma_1 \rightarrow \Gamma_4$, $\Gamma_3 \rightarrow \Gamma_4$, $\Gamma_3 \rightarrow \Gamma_5$, and $\Gamma_4 \rightarrow \Gamma_5$ are allowed. The relative intensities may be simply calculated using Eq. (1) and the eigenstates tabulated by LLW.

The experiments were carried out on the "slow chopper" neutron time-of-flight spectrometer at the Brookhaven high-flux beam reactor. The incident neutrons had a wavelength of 4.1 Å corresponding to an energy of 4.9 meV. All experiments were carried out in the energy gain configuration; that is, the Pr^{3+} ion is de-excited from a higher to a lower state and the neutron gains the corresponding energy. The samples were polycrystalline ingots approximately 2 cm^3 in volume. Typical counting times were 20 h for each sample at each temperature. Data were collected in sets of 6, 5, and 3 counters spaced about 1° apart with their centroids at 27°, 42°, and 99°, respectively, from the forward direction. For typical energy transfers these give momentum transfers ranging from $|Q| \sim 1.5$ to 3.2 Å^{-1} so that the conditions for the validity of Eq. (1) should be well satisfied.[9] In addition, the Q dependence of the peak intensities is automatically determined.

Typical experimental spectra for PrSb are shown in Fig. 1. At 80°K the spectrum is dominated by one very intense peak at 6.4 ± 0.5 meV with a shoulder on the low-energy side at 4.5 ± 0.5 meV and two weaker peaks at 9.5 ± 0.6 and 14.8 ± 1.0 meV. When the temperature is increased to 295°K, the two upper peaks increase in intensity by about a factor of 4; the (6.4 ± 0.5)-meV peak decreases in peak height but broadens considerably. This broadening is consistent with assuming a marked increase in intensity for the shoulder at 4.5 ± 0.5 meV observed at 80°K together with some intrinsic line broadening. Comparison of the relative intensities from the three groups of counters shows that all four observed peaks arise from crystal-field rather than phonon processes.

Analysis of the PrSb spectra is quite straightforward. Susceptibility and specific-heat measurements indicate that the Γ_1 singlet lies lowest. The peak at 6.4 meV may then be identified
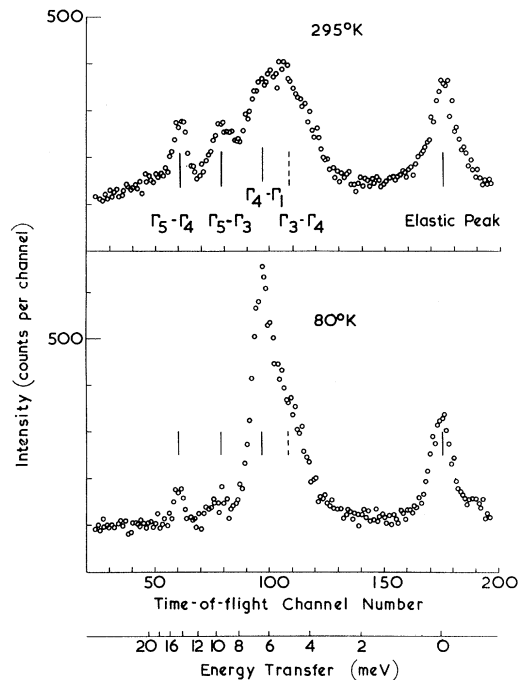
FIG. 1. Time-of-flight neutron spectra for PrSb at 80 and 295°K.

as the $\Gamma_4 \rightarrow \Gamma_1$ transition. From LLW it is found that for all values of the parameters, $\Delta E(\Gamma_3 - \Gamma_4) = (5/7)\Delta E(\Gamma_4 - \Gamma_1)$ so that the shoulder at 4.5 meV is the $\Gamma_3 \rightarrow \Gamma_4$ transition. The two outer transitions may then be immediately identified as $\Gamma_5 \rightarrow \Gamma_4$ and $\Gamma_5 \rightarrow \Gamma_3$. This gives $E(\Gamma_4) = 6.4 \pm 0.5$ meV, $E(\Gamma_3) = 11.9 \pm 0.5$ meV, and $E(\Gamma_5) = 21.2 \pm 1.5$ meV with all four transitions properly accounted for. The corresponding crystal-field parameters are given in Table I. Calculations also show that relative intensities at both 295 and 80°K are well accounted for using the above level

scheme. It is interesting to note that the total intensity of the $\Gamma_4 \rightarrow \Gamma_1$ transition actually increases in going from 295 to 80°K whereas it would have decreased by a factor of 5 if it arose from one-phonon scattering. It should also be noted that both the inelastic paramagnetic scattering around the elastic peak at 295°K and the narrow width of the $\Gamma_5 \rightarrow \Gamma_4$ transition shows that the exchange is small compared with the crystal-field energies.

Spectra similar to those given for PrSb in Fig. 1 are observed in the other praseodynium pnictides and chalcogenides. The crystal-field parameters for the compounds we have studied are listed in Table I.[13] There are a number of rather unexpected features. Firstly, the crystal field is almost entirely fourth order; there is no apparent enhancement of the sixth-order terms as usually occurs in insulators as a result of overlap and covalency.[5,14] Secondly, there is no appreciable difference between the Va and VIa compounds; indeed, the lattice constant seems to be the only significant parameter. Thirdly, the fourth-order terms are found to follow a simple R^{-5} law with an absolute magnitude which is quite close to that calculated using a nearest-neighbor point-charge model with a charge of -2 at the ligand site. These results may be restated as follows: All of the crystal-field levels in all seven compounds can be quantitatively accounted for by use of a nearest-neighbor point-charge model with an effective charge of -2. The mean deviation using this model is 10% and, in fact, the majority of the levels are fitted to within the experimental error. This is a remarkable result especially when one considers that the model is of little quantitative value in rare-earth insula-

Table I. Crystal field parameters in prasedymium chalcogenides and pnictides.[a]

	Lattice constant[b] (Å)	$A_4 \langle r^4 \rangle$ (meV)	$A_6 \langle r^6 \rangle$ (meV)		Lattice constant[b] (Å)	$A_4 \langle r^4 \rangle$ (meV)	$A_6 \langle r^6 \rangle$ (meV)
PrBi[c]	6.461	6.9 ± 0.4 (7.9)	0.24 ± 0.10 (0.13)				
PrSb	6.376	8.6 ± 1.0 (8.4)	0.17 ± 0.12 (0.14)	PrTe	6.320	9.1 ± 1.3 (8.8)	0.16 ± 0.19 (0.15)
PrAs	6.030	12.6 ± 0.9 (11.2)	0.39 ± 0.18 (0.20)	PrSe	5.942	12.7 ± 0.7 (12.0)	0.49 ± 0.19 (0.23)
PrP	5.905	13.7 ± 0.4 (12.5)	0.47 ± 0.10 (0.24)	PrS	5.735	13.8 ± 1.6 (14.2)	0.72 ± 0.24 (0.29)

[a]The point-charge–model values for the parameters are given in parentheses.
[b]A. S. Cooper, unpublished.
[c]R. J. Birgeneau et al., J. Appl. Phys. 41, 900 (1970).

tors such as $PrCl_3$.[5,14] Indeed, one would have expected that all of the mechanisms operative in insulators, that is, $4f$-ligand overlap and covalency, point-charge effects, charge penetration, $5s5p$ shielding, and charge redistribution,[5] would be present in the chalcogenides and pnictides; in addition, one has the complication of possible shielding and $5d$ virtual bound-state effects[15] arising from the conduction electrons. Furthermore, we, at least, had anticipated that these effects would manifest themselves differently in the chalcogenides and pnictides. In particular, the fact that corresponding chalcogenides and pnictides have virtually identical crystal fields whereas the conduction-electron concentrations differ considerably indicates that the conduction electrons are ineffective both in terms of simple screening and in terms of $5d$ crystal-field effects.[16] We have not, as yet, come to any satisfactory understanding of why the Stark splittings in these metallic compounds do not seem to reflect the anticipated complications.

We should like to acknowledge stimulating conversations with M. Blume, W. F. Brinkman, A. M. Clogston, and R. E. Watson.

[1]R. J. Elliott, in *Magnetism,* edited by G. T. Rado and H. Suhl (Academic, New York, 1965), Vol. 2A, p. 385. See also S. Methfessel and D. C. Mattis, in *Handbuch der Physik,* edited by S. Flügge (Springer, New York, 1968), Vol. XVIII/1, p. 389.

[2]The main experimental technique employed has been measurements of the bulk susceptibility and specific heat on polycrystalline materials; although these give very useful information, it is only rarely that they can be used to obtain unambiguous values for all of the parameters in the crystal-field Hamiltonian. See, for example, K. H. J. Buschow, H. W. de Wijn, and A. M. van Diepen, J. Chem. Phys. 50, 137 (1969); B. R. Cooper

and O. Vogt, Phys. Rev. B 1, 1211 (1970); B. Bleaney, Proc. Roy. Soc., Ser. A 276, 39 (1963); G. Busch, J. Appl. Phys. 38, 1386 (1967).

[3]R. J. Elliott, Comments Solid State Phys. 1, 85 (1968).

[4]G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals* (Wiley, New York, 1968).

[5]M. M. Ellis and D. J. Newman, J. Chem. Phys. 49, 4937 (1968), and references contained therein.

[6]B. D. Rainford, K. C. Turberfield, G. Busch, and O. Vogt, J. Phys. C: Proc. Phys. Soc., London 1, 679 (1968), for earlier work in insulators, see D. Cribier and B. Jacrot, C. R. Acad. Sci. 250, 2871 (1960); B. N. Brockhouse, L. N. Becka, K. R. Rao, R. N. Sinclair, and A. D. B. Woods, J. Phys. Soc. Jap. 17, Suppl. B-III, 63 (1962).

[7]M. T. Hutchings, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 227.

[8]G. T. Trammell, Phys. Rev. 92, 1387 (1953).

[9]D. F. Johnston, J. Phys. A: Proc. Phys. Soc., London 88, 37 (1966); E. Balcar and S. W. Lovesey, Phys. Lett. 31A, 67 (1970).

[10]If there are appreciable exchange interactions between the ions then Eq. (1) is no longer sufficient; at low temperatures one must carry out a summation over the lattice sites with the matrix elements of $J_\perp(\vec{r}_i)$ evaluated between Bloch-wave crystal-field excitons [B. R. Cooper, J. Appl. Phys. 40, 1344 (1969)]. At higher temperatures the situation will be even more complicated.

[11]See, for example, F. Hulliger, Helv. Phys. Acta 41, 945 (1968), and references contained therein; D. E. Eastman, F. Holtzberg, and S. Methfessel, Phys. Rev. Lett. 23, 226 (1969).

[12]K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids 23, 1381 (1962).

[13]The crystal-field energies were obtained directly from the peak positions; proper deconvolution of the instrumental resolution may cause changes of a few percent but these should all be well within the quoted errors.

[14]M. T. Hutchings and D. K. Ray, Proc. Phys. Soc., London 81, 663 (1963).

[15]G. Williams and L. L. Hirst, Phys. Rev. 185, 407 (1969).

[16]Williams and Hirst, Ref. 14, calculate the $5d$ effects to be of the same order of magnitude as the point charge contributions but of opposite sign.