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# Crystal Field Potential of $NdCu_2Si_2$: A Comparison with $CeCu_2Si_2$

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## Abstract

The results of an inelastic neutron scattering investigation of the crystal field potential of $NdCu_2Si_2$ are reported. We have observed three ground state and three excited state transitions which establish unambiguously the crystal field level scheme with an overall splitting of 11.45 meV. By performing a profile refinement of the measured spectra we have determined the Hamiltonian parameters for the tetragonal crystal field: $B_2^0 = (-3.1 \pm 0.1) \times 10^{-2}$ meV, $B_4^0 = (1.1 \pm 0.1) \times 10^{-3}$ meV, $B_4^4 = (1.33 \pm 0.04) \times 10^{-3}$ meV, $B_6^0 = (-3.17 \pm 0.04) \times 10^{-5}$ meV and $B_6^4 = (6.62 \pm 0.02) \times 10^{-4}$ meV. The parameters are analysed in terms of Newman's superposition model and compared to recent results on the isostrucutural heavy fermion compound $CeCu_2Si_2$.

Keywords: Crystal Field, Neutron Scattering, Heavy Fermion

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## 1. Introduction

There has been considerable interest in the $RCu_2Si_2$ series of isostructural compounds, where R represents a rare-earth element, since the discovery of heavy fermion superconductivity in $CeCu_2Si_2$ [1], and intermediate valence in $EuCu_2Si_2$ and $YbCu_2Si_2$ [2]. As with all rare-earth systems, a key role in determining the magnetic and thermodynamic properties of these compounds is played by the interaction of the f-electrons with the crystal field (CF) potential produced by the local lattice environment [3] so it is perhaps surprising that there has been no determination of the CF across this series. It is particularly important to study the CF of normal rare earth compounds in order to establish the degree to which the potential is anomalous in compounds with unstable f-shells. Levy and Zhang [4] have proposed that, in heavy fermion compounds, the hybridization between the f-shell and the ligand electronic orbitals, which gives rise to the heavy fermion properties, is also the dominant component in the CF potential. A comparison of the CF in $CeCu_2Si_2$ with other normal $RCu_2Si_2$ compounds can establish the validity of this proposal and help to clarify the nature of these hybridization interactions. An additional reason for investigating the CF is that members of this series display unusual magneto-elastic anisotropy at low temperature [5], which can only be understood when the CF potential is known.

The most reliable method of determining the CF potential is inelastic neutron scattering (INS) which measures directly the energies and dipole matrix elements of transitions between CF levels [3]. We have recently derived the CF parameters for $CeCu_2Si_2$ [6] which, following an analysis using Newman's superposition model (SM) [7], show evidence for a strong hybridization between the cerium f-electrons and the silicon ion valence electrons. In order to see if this observation is anomalous in the context of the other $RCu_2Si_2$ compounds, we have begun a systematic investigation of the CF potential in this isostructural series. The present article reports the results of an INS determination of the CF parameters in $NdCu_2Si_2$ which we then compare to those of $CeCu_2Si_2$ in the framework of the SM.

## 2. Experimental Details and Results

The sample of $NdCu_2Si_2$ was prepared by arc-melting stoichiometric quantities of the constituent elements, with no measurable weight loss. After annealing at 700°C, both neutron and X-ray diffraction confirmed that the sample contained no other phases. After preliminary measurements on the neutron spectrometer KDSOG, at the pulsed reactor IBR-2 (Dubna, Russia), higher resolution INS were performed on the time-of-flight chopper spectrometer HET, at the pulsed spallation neutron source ISIS (Rutherford Appleton Laboratory, U.K.) using incident energies of 15 meV and 25 meV with resolutions at the elastic position of 0.4 meV and 0.75 meV respectively. About 50g of the sample was sealed in an aluminium-walled can and mounted on a closed-cycle refridgerator for scans at 20K, 30K and 50K.

The INS spectra summed over scattering angles from 10° to 30° at the three measured temperatures are shown in Fig. 1. Comparison with spectra taken at 136° where the nuclear scattering is strongest confirm that the phonon contribution is negligible at low angles in this energy range.

Inspection of the data shows that at high temperature there are four main excitation bands in down-scattering at about 3, 4, 6 and 11 meV (Fig. 1(a)). At 20K, measured with lower incident energy, these bands can be resolved into six peaks at energy transfers of 2.8, 4.0, 4.8, 6.0, 10.5 and 11.6 meV. There is evidence for intrinsic broadening of these peaks since the linewidths are greater than the resolution and the profiles are well described by Lorentzian lineshapes. We excluded the energy transfer range from -2.5 to 2.0 meV in subsequent analysis because the elastic peak contains strong nuclear scattering contributions.

## 3. Data Analysis and CF Model

The neodymium ions in $NdCu_2Si_2$ sit on lattice sites with tetragonal point symmetry, so the CF Hamiltonian is

$$\mathcal{H} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4 \qquad (1)$$

where $O_n^m$ are the Steven's operator equivalents and $B_n^m$ are the phenomenological CF parameters. This splits the J=9/2 ground state multiplet of the $Nd^{3+}$ ion into five Kramers doublets.

The neutron scattering cross section for transitions between these CF levels is given by [3]

$$\frac{d^2\sigma}{d\Omega d\epsilon} \propto \frac{k_f}{k_i} f^2(Q) \exp(-2W) \sum_{ij} p_i |\langle j|J_\perp|i\rangle|^2 F(\epsilon - \epsilon_{ij}, \Gamma_{ij}) \qquad (2)$$

where $k_i$ and $k_f$ are the incident and final neutron wavevectors, $f^2(Q)$ is the f-electron form factor as a function of wavevector transfer $Q$, exp(-2$W$) is the Debye-Waller factor, $p_i$ is the occupation probability of the CF level |i> with energy $\varepsilon_i$, $J_\perp$ is the component of the total angular momentum perpendicular to the scattering plane and $F(\varepsilon-\varepsilon_{ij},\Gamma_{ij})$ is the lineshape function for a peak at energy transfer centred at $\varepsilon_{ij} = \varepsilon_i - \varepsilon_j$ with a half-width $\Gamma_{ij}$. In the present work, we have found that only Lorentzian functions described the observed peak lineshapes adequately.

As mentioned in the previous section, we have observed six transitions at 20K whereas there are only four possible transitions from the ground state. There must therefore be a low-lying level which is substantially populated at 20K. Although we have not directly observed a ground state transition to this level, we can infer its energy by noting that the six measured peaks may be grouped into three pairs, with the members of each pair separated by about 1.2 meV. We therefore assume that the missing level is at 1.2 meV with the remaining three levels at 4.0, 6.0 and 11.6 meV. This assumption is consistent qualitatively with the observed temperature dependence of the six peaks.

There is no way to estimate the CF parameters of $NdCu_2Si_2$ *a priori* since the CF potential of $CeCu_2Si_2$ may be anomalous and, in any case, provides no values for the sixth-degree parameters. We have therefore made a comprehensive survey of the allowed parameters using the modified parametrization of the CF Hamiltonian due to Walter [8].

$$\mathcal{H} = W\left[\left(1 - |x_1| - |x_2| - |x_3| - |x_4|\right)O_2^0 + x_1\frac{O_4^0}{60} + x_2\frac{O_4^4}{12} + x_3\frac{O_6^0}{1680} + x_4\frac{O_6^4}{240}\right] \qquad (3)$$

The modified CF parameters $x_i$ are subject to the following constraint $\sum_{i=1}^{4} x_i \leq 1$ so restricting the range of allowed parameter values. If the full splitting is known, $W$ is fixed each set of the $x_i$ parameters. The observed positions and intensities of the CF peaks are only consistent qualitatively in a small region of parameter space within which the model was refined by least-squares fitting the measured profiles at 20K. The resulting parameters are $W$ = -0.325 meV, $x_1$ = -0.203, $x_2$ = -0.049, $x_3$ = 0.164, $x_4$ = -0.489. The corresponding $B_n^m$ are listed in Table 1 and the CF level scheme and wavefunctions are shown in Fig. 2. We also list the values of $A_n^m$, defined by $B_n^m = \Theta_n A_n^m \langle r^n \rangle$ where $\Theta_n$ are the Steven's factors and $\langle r^n \rangle$ are the f-electron radial integrals, in order to facilitate comparison with $CeCu_2Si_2$.

The solid lines in Fig. 1 represent the results of the profile refinement of the magnetic scattering using this CF model, with the individual CF transitions shown by the dashed lines. It can be seen that the model describes well the evolution with temperature of all the transitions. A common linewidth was used for all transitions at each temperature; $\Gamma$ = (0.30 ± 0.02) meV at 20K, (0.037 ± 0.02) meV at 30K and (0.048 ± 0.08) meV at 50K.

There are a few minor discrepancies between the calculated and measured spectra although the overall agreement is very good for a CF-only model. It is probable that the intensity distribution above 10 meV could be described better by allowing different linewidths for the two peaks at 10.2 meV and 11.45 meV as would occur if we used the Becker-Fulde-Keller model of exchange broadening [9]. However, we believe there is a contribution to the measured linewidth and peak position from dispersion of these CF exciton branches, since we have observed shifts of 0.5 meV in the ground state transition at 3.89 meV (Fig. 2) when Q increases from 0.45 $Å^{-1}$ to1.2 $Å^{-1}$. There is also evidence of dispersion in this CF level from a shift in the energy one of the excited state transitions. The peak, arising from the transition from the 3.89 meV to the 11.45 meV level (Fig. 2) *i.e.* expected to be at 7.56 meV, is instead observed at 8.1 meV (Fig. 1(a,b)). The other transitions do not show such

large shifts, but above 8 meV, the Q-variation in the measured angular range of 3° to 30° is too small for dispersion effects to be observed.

## 4. Superposition Model and Comparison with $CeCu_2Si_2$

The CF potential of $NdCu_2Si_2$ is substantially different from $CeCu_2Si_2$ . Table 1 shows that the magnitudes of the CF parameters differ by factors of between 4 and 10, even after correction for the reduction of the 4f-electron radial integrals of the neodymium ion *i.e.* the $A_n^m$ values. This result cannot be explained by the compression of the lattice in $NdCu_2Si_2$, since the rare earth-ligand distances decrease by less than 1%. Furthermore, there is a large difference in the ratios of two $4^{th}$-degree CF parameters, with $B_4^0$ considerably larger and $B_4^4$ considerably smaller in $NdCu_2Si_2$, which suggests that there is a fundamental difference in the origin of the CF in the two compounds. In order to understand this observation, it is necessary to separate the geometrical coordination factors from the intrinsic strength of the potential in the CF parameters. For this, we have used the SM [7] which assumes that the CF is the superposition of two-body potentials due to the nearest-neighbour ions alone. Newman and Ng [7] have discussed the validity of neglecting contributions from more distant neighbours, and concluded that the approximation works very well for the $4^{th}$ and $6^{th}$ degree parameters but is less reliable for the $2^{nd}$ degree parameters. Although the best evidence for these conclusions comes from ionic compounds, it has been argued that the potential of more distant shells will be even more efficiently screened in metallic systems [10,11]. Newman and Ng have also shown that nearly all contributions to the CF potential, including overlap and hybridization (covalency), obey the superposition principle.

In the SM, the CF potential is expressed in terms of the three SM parameters $\bar{A}_2$, $\bar{A}_4$ and $\bar{A}_6$ which represent the cylindrically symmetric potential between the rare earth ion and each ligand. They are related to the $B_n^m$ by

$$B_n^m = \Theta_n \sum_i \bar{A}_n(R_i) K_{mn}(\theta_i, \phi_i) \qquad (4)$$

where the sum is over the nearest-neighbour ligands at $(R_i, \theta_i, \phi_i)$. In the present example, the CF parameters contain contributions from both the nearly equidistant shells of eight copper and eight silicon ions. Using the lattice parameter of Schlabitz *et al* [5], the copper and silicon shells are at 3.209 Å and 3.113 Å respectively. and the corresponding SM equations are given by the following formulae

$$\begin{aligned} B_2^0 &= \Theta_2\left(3.187\overline{A}_2^{Cu} - 2.226\overline{A}_2^{Si}\right) \\ B_4^0 &= \Theta_4\left(-2.413\overline{A}_4^{Cu} - 0.670\overline{A}_4^{Si}\right) \\ B_4^4 &= \Theta_4\left(5.631\overline{A}_4^{Cu} - 25.418\overline{A}_4^{Si}\right) \\ B_6^0 &= \Theta_6\left(-2.739\overline{A}_6^{Cu} + 2.192\overline{A}_6^{Si}\right) \\ B_6^4 &= \Theta_6\left(28.318\overline{A}_6^{Cu} - 14.319\overline{A}_6^{Si}\right) \end{aligned} \qquad (5)$$

The 2nd and 4th degree equations are slightly different from those in Ref. 6 for $CeCu_2Si_2$ because of the small change in the c/a ratio.

Since the SM equations are less reliable for $B_2^0$, we concentrate the subsequent comparison on $B_4^0$ and $B_4^4$ and, in particular, the ratio $B_4^4/B_4^0$. In $NdCu_2Si_2$ and $CeCu_2Si_2$, the measured ratios are 1.2 and 104 respectively. Eqn 5 shows that the copper CF would on its own produce a ratio of -2.3 whereas the silicon CF ratio is 37.9 because of the different polar angles of the two ligand shells, 39.3° and 67.4° for the copper and silicon neighbours respectively. $K_4^4$ is proportional to $\sin^4\theta$ and therefore larger for silicon than copper. On the other hand, $K_4^0$ has a more complicated dependence on $\theta$ and falls to 0 at $\theta = 70.1°$, close to the silicon sublattice angle. A large (small) ratio therefore implies that the silicon (copper) contribution is predominant in the CF potential.

The qualitative conclusion, based on the present experiment, is therefore that the CF potential is dominated by the copper sublattice in $NdCu_2Si_2$ and the silicon sublattice in $CeCu_2Si_2$. This is confirmed by the values of $\overline{A}_4^{Cu}$ and $\overline{A}_n^{Si}$ in Table 1. These were obtained from Eqn 5 with two possible solutions corresponding to different signs for $B_4^4$

and $B_6^4$. These are not fixed because the CF peak positions and intensitites are unchanged by the simultaneous change of sign of both parameters.

In $NdCu_2Si_2$, both solutions give $\bar{A}_4^{Cu}$ ~ 1.5 meV with smaller values for $\bar{A}_4^{Si}$. The magnitude of $\bar{A}_4^{Si}$ is then increased by at least a factor 5 in $CeCu_2Si_2$. Since the normal contributions to the CF are not expected to vary significantly between the two compounds, the increase is probably related to the greater hybridization of the f-electrons in the cerium compound, since this also produces their anomalous heavy fermion properties, and suggests that the silicon valence electrons make the predominant contribution to this hybridization. We therefore assume that the copper CF is not anomalous. The solution with $\bar{A}_4^{Cu} > 0$ in $CeCu_2Si_2$ is to be preferred since it has the same sign as in $NdCu_2Si_2$ and the evidence of all other rare earth intermetallic compounds studied so far [10,12] is that $\bar{A}_4$ is always positive (*N.B.* they are positive in both solutions for $NdCu_2Si_2$). This solution is consistent with a modest fall in the copper CF with the expansion of the lattice but has the unexpected consequence that $\bar{A}_4^{Si}$ is negative. Most normal contributions to the CF have a positive sign *i.e.* the f-electron-ligand potential is repulsive, but it is not unreasonable to suppose that the hybridization interaction, that stabilizes the non-magnetic Fermi liquid state, produces an attractive potential.

Both signs for $B_4^4$ and $B_6^4$ give reasonable values for $\bar{A}_4^{Cu}$ and $\bar{A}_4^{Si}$ in $NdCu_2Si_2$ but predict different signs for the $6^{th}$-degree parameters. The evidence of other intermetallic compounds is more equivocal in the case of $\bar{A}_6$ since negative values are sometimes found probably because of the greater influence of charge interpenetration on these parameters [10]. Indeed, the negative solution seems more likely since the magnitude of $\bar{A}_6$ is usually smaller than $\bar{A}_4$. However, in intermetallic compounds. the higher-degree parameters seem to depend more sensitively on the strengths of a number of contributions with competing signs, so it is not possible to draw any conclusions from just one measurement. We are in the process of investigating the CF potential of other $RCu_2Si_2$ compounds in order to establish the systematic trends in all the CF parameters.

Finally, we remark on the sign of $B_2^0$ which usually defines the magnetic anisotropy (easy axis or easy plane). Although the magnetic structure of $NdCu_2Si_2$ has not yet been determined, it has been inferred both from lattice parameter anomalies in $NdCu_2Si_2$ [5] and the results of neutron diffraction measurements on other $RCu_2Si_2$ compounds [13] that the moment should lie in the plane, which implies that $B_2^0$ should be positive in contradiction to our observation. However, the anisotropy is very small in this compound and, according to our CF model, the easy direction of the moment changes from easy axis at high temperature to easy plane below 17.6 K. In other words, the anisotropy is not completely determined by the sign of $B_2^0$ as often assumed but depends on the whole CF Hamiltonian.

## 5. Conclusions

The $RT_2X_2$-series of isostructural compounds provide a particularly useful to investigate the origin of the CF in both normal rare earth intermetallic compounds, for which there are still no reliable *ab initio* calculations, and heavy fermion compounds, in which there may be an intimate link between the CF potential itself and the anomalous f-electron hybridization. In this article, we have derived the CF potential of $NdCu_2Si_2$ from the results of inelastic neutron scattering, from which the complete level scheme could be deduced from the observation of both ground state and excited state transitions. The peak positions and intensities define the CF potential unambiguously although a more precise refinement would need to take into account the dispersion of the CF levels by interionic exchange. A superposition model analysis of the CF parameters indicates that the copper ligands make the larger contribution to the $4^{th}$-degree parameters and there are approximately equal contributions from the copper and silicon ligands to the $6^{th}$-degree parameters. In contrast, the silicon ligands make the larger contribution to the $4^{th}$degree parameters with an anomalous sign in $CeCu_2Si_2$. We suggest that there is an important contribution to the CF from f-electron hybridization with the silicon valence electrons in the heavy fermion compound, in line with theoretical prediction [4]. The CF is therefore throwing light on the nature of the hybridization interactions that produce the heavy fermion properties of $CeCu_2Si_2$.

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## Tables

Table 1 Experimental values of the Crystal Field parameters of $NdCu_2Si_2$ and $CeCu_2Si_2$ and the result of the Superposition Model analysis.

| n | m | $B_n^m$ (meV) | $A_n^m$ (meVÅ$^{-n}$) | $\bar{A}_n^{Cu}$ (meV) | $\bar{A}_n^{Si}$ (meV) |
|---|---|---|---|---|---|
| | | $NdCu_2Si_2$ | | | |
| 2 | 0 | $-(3.1 \pm 0.1) \times 10^{-2}$ | 15.46 | - | - |
| 4 | 0 | $(1.1 \pm 0.1) \times 10^{-3}$ | -18.75 | | |
| 4 | 4 | $(1.33 \pm 0.04) \times 10^{-3}$ | -22.67 | 1.52 | 0.16 |
| | | $-(1.33 \pm 0.04) \times 10^{-3}$ | 22.67 | 1.43 | 0.50 |
| 6 | 0 | $-(3.17 \pm 0.04) \times 10^{-5}$ | 2.53 | | |
| 6 | 4 | $(6.62 \pm 0.02) \times 10^{-4}$ | -52.81 | 2.20 | 3.14 |
| | | $-(6.62 \pm 0.02) \times 10^{-4}$ | 52.81 | -1.15 | -1.05 |
| | | $CeCu_2Si_2$ | | | |
| 2 | 0 | $-(1.29 \pm 0.01)$ | 61.58 | - | - |
| 4 | 0 | $-(4.34 \pm 0.03) \times 10^{-3}$ | -2.20 | | |
| 4 | 4 | $0.453 \pm 0.003$ | 229.56 | 0.943 | -2.58 |
| | | $-0.453 \pm 0.003$ | -229.56 | -0.417 | 2.69 |

## Figures

Figure 1 Neutron inelastic scattering from $NdCu_2Si_2$ at an average scattering angle of 20° with temperatures and incident energies of (a) 50 K and 25 meV, (b) 30 K and 25 meV, and (c) 20 K and 15 meV. The solid line is the profile of the CF model refined at 20 K. The dashed lines are the separate CF transitions.

Figure 2 The CF level scheme and f-electron wavefunctions of $Nd^{3+}$ ion in $NdCu_2Si_2$ determined from the CF model of Table 1.

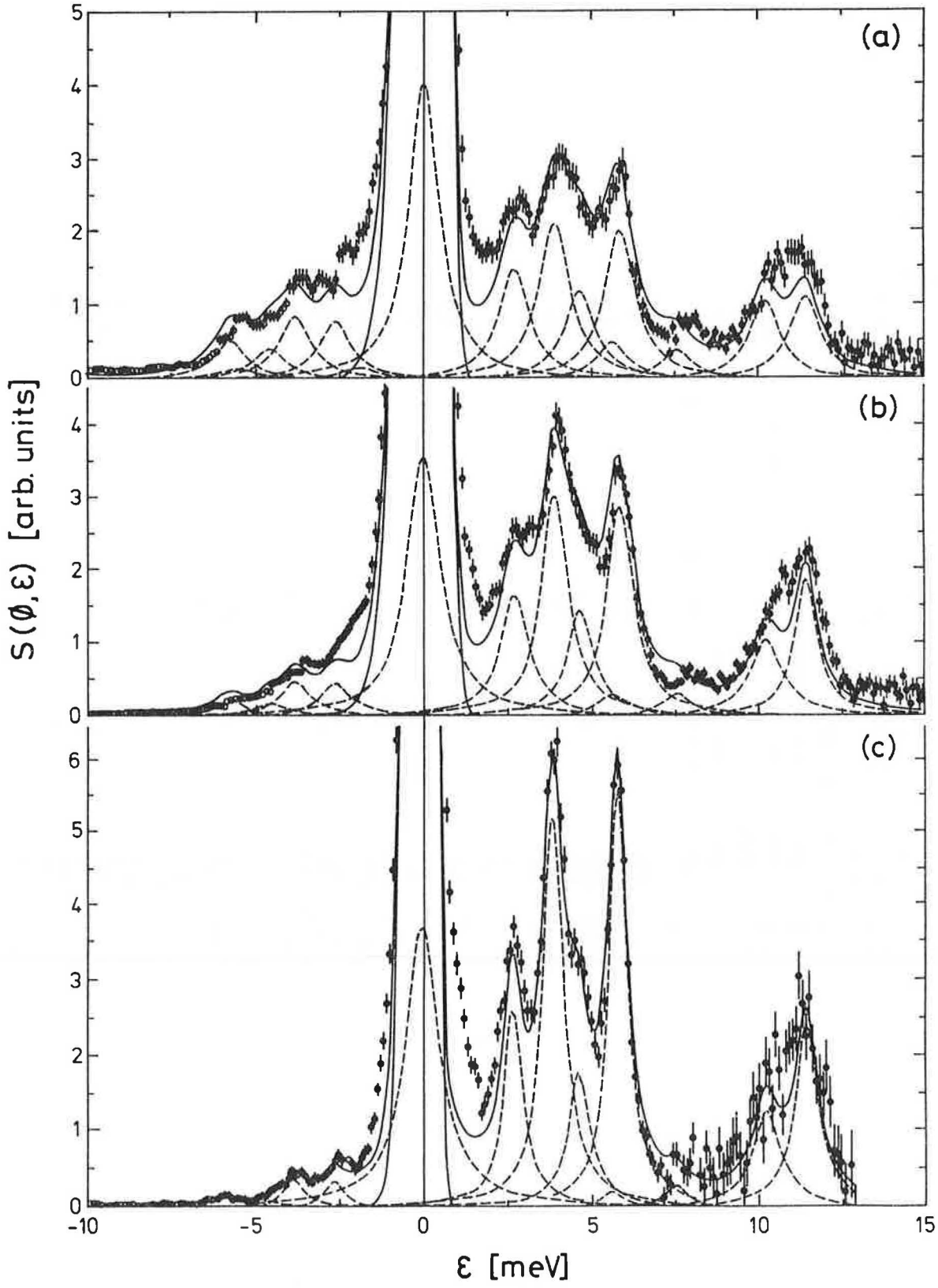


Figure 1

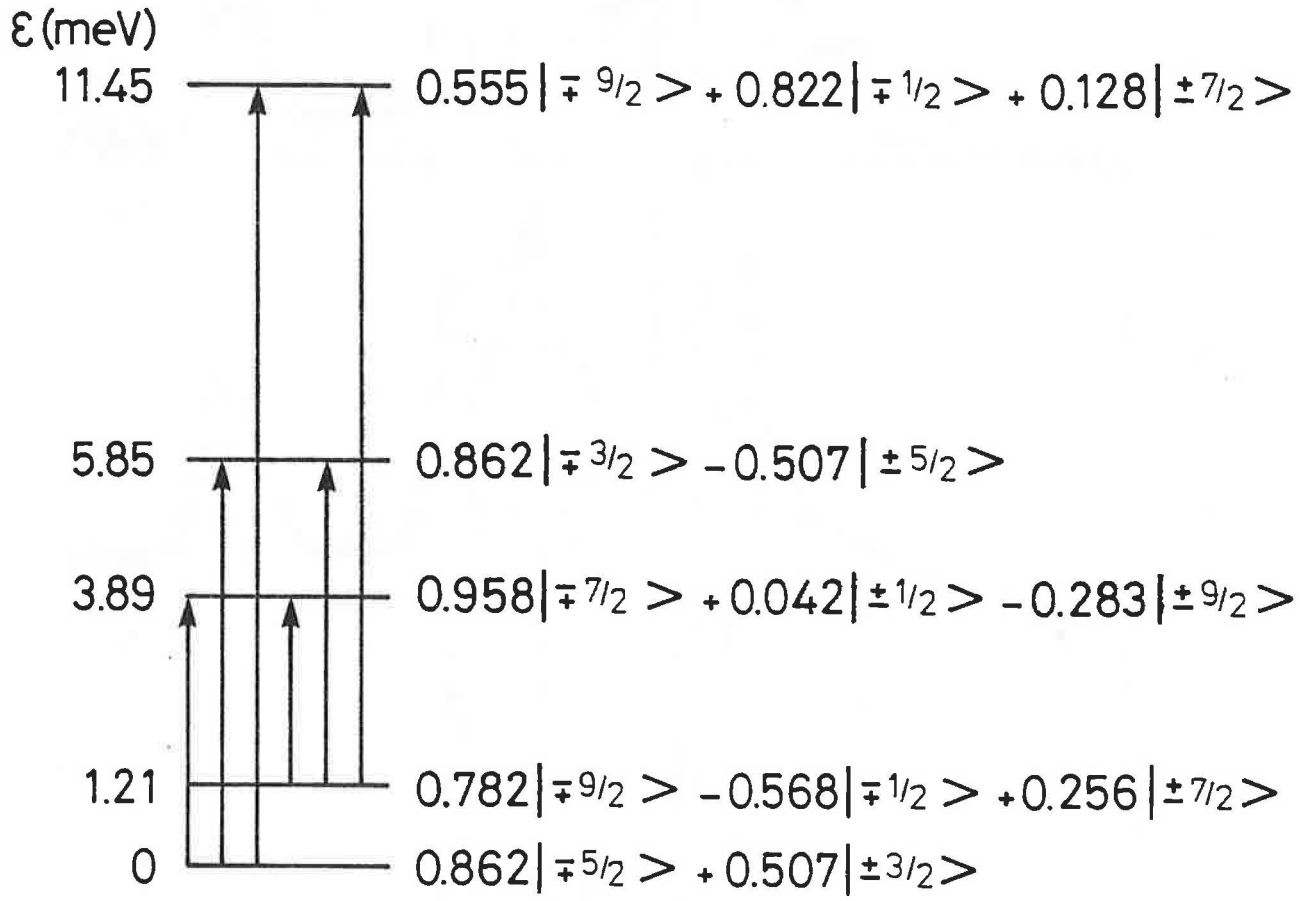
ε (meV)
11.45
0.555|∓9/2> + 0.822|∓1/2> + 0.128|±7/2>
5.85
0.862|∓3/2> − 0.507|±5/2>
3.89
0.958|∓7/2> + 0.042|±1/2> − 0.283|±9/2>
1.21
0.782|∓9/2> − 0.568|∓1/2> + 0.256|±7/2>
0
0.862|∓5/2> + 0.507|±3/2>

Figure 2