Referee report on the doctoral thesis of Jiri Prchal, entitled:

"Study of magnetic properties of $RT^1_{1-x}T^2_xX$ compounds".

This doctoral thesis is primarily focused on the interesting magnetic behavior of the pseudo-ternary series Dy(Ni,Cu)Al and Er(Ni,Cu)Al with emphasis on the quite interesting evolution of magnetic order and magnetocrystalline anisotropy upon going from one parent compound to the other. To this end, polycrystalline samples with the proper ZrNiAl-type of crystal structure have been prepared with great care and a single crystal of DyNiAl has been grown. The quality of the prepared samples has been thoroughly checked by microprobe analysis and X-ray diffraction, establishing that they have crystallized single-phase in the ZrNiAl structure. Additional refinement of the crystal structure at low temperatures was carried out by means of neutron diffraction. The physical, predominantly magnetic, properties of the prepared compounds have been determined in much detail by means of a large variety of the most advanced experimental microscopic and macrocopic experimental techniques. Particularly, neutron-diffraction experiments, which provide indispensable information on the magnetic structure, constitute an important and essential part of the work, particularly in the determination of the complex magnetic structures of the pseudo-ternary compounds.

A second, equally important, part of the thesis concerns a structural study of (quasi)ternary compounds. A structural study of the Dy(Ni,Cu)Al series has revealed, similar to what has been found earlier for the Er(Ni,Cu)Al and Tb(Ni,Cu)Al series, a very intriguing transition from a crystal structure with "high" c/a ratio (for Cu-rich compounds) to one with "low" c/a ratio (for Ni-rich compounds) which gives rise to the tempting idea of the existence of an interval with "forbidden" c/a ratio. Besides the discovery of this "c/a transition" as a function of Ni-Cu ratio, another very interesting result in this thesis is the observation of the occurrence of the same "c/a transition" if the temperature is varied. This transition was not only found in the Er(Ni,Cu)Al and Tb(Ni,Cu)Al series, but also in several other ternary and pseudo-ternary compounds crystallizing the ZrNiAl structure. Somewhat unexpected, there is no observable volume anomaly associated with the transition. In the (Ce,Y)PdAl and Tb(Pd,Ni)Al series, the transition is not found which poses some doubt on the concept of the "forbidden" c/a ratio in these compounds. However, these deviations are discussed in the thesis and further experiments are needed to show that, as proposed in the thesis, these exceptions do not violate this concept.

It would be very much appreciated by the referee if the following comments and questions would be addressed:

Comment 1:

In the thesis, it is concluded that it has not been possible to establish a general relationship between the magnetic properties (magnetic structure, etc.) of the thoroughly investigated quasi-ternary compounds and their observed "c/a phase". Nevertheless it may be expected that, for a specific compound, the magnetic properties will be appreciably different for the "low c/a" phase and for the "high c/a" phase. It is mentioned on p. 54 that the quality of the $DyNi_{0.7}Cu_{0.3}Al$ sample is very low which is attributed to the vicinity of the c/a transformation. Since the neutron-diffraction pattern of $DyNi_{0.7}Cu_{0.3}Al$ is not included in Fig. 5.30 and therefore not discussed, it would be interesting to know what is exactly wrong with the sample, for instance whether both c/a phases are present or possibly other phases. In addition, because concentration fluctuations are inevitably present in the investigated compounds, the question arises immediately whether the quality of other samples that are not very far from the c/a transformation, for instance $DyNi_{0.8}Cu_{0.2}Al$ and $DyNi_{0.6}Cu_{0.4}Al$, also may be affected to some extent by the proximity of the phase transformation, of course much less than $DyNi_{0.7}Cu_{0.3}Al$ that appears to be approximately at the phase transition. In the cases of $DyNi_{0.8}Cu_{0.2}Al$ and $DyNi_{0.6}Cu_{0.4}Al$, one might particularly think of the occurrence of small regions in the sample in which, due to fluctuations in the concentration, both c/a phases may be present, not in sufficient amount to be both detected by X-ray or neutron diffraction, but enough to cause strains in the sample which may obscure the observation of the intrinsic single c/a phase magnetic properties. Have any indications of less optimal quality been found in practice for the samples with composition not very far from the "c/a transition"?

Comment 2:
It seems that in the investigation of the "c/a transformation" in the various systems, no specific-heat measurements have been carried out. Such measurements would be of prime interest because they provide information on the entropy change involved and may, for instance, give an indication whether there is only a difference in vibrational entropy between the two states or whether atomic disorder may be involved in one of the two states. Why have such measurements not been done?

Comment 3:
As mentioned on page 58, the "c/a transformation" must be related to the atomic bonding forces within the basal planes and between the planes. The referee agrees with this. Which possibilities can be thought of to further investigate this transition experimentally or theoretically and to come eventually to a theoretical description?

In conclusion, the interesting experimental results presented by Jiri Prchal in this doctoral thesis and the theoretical interpretation that he has given, clearly demonstrate that he is able to carry out scientific research in an independent way.

Amsterdam, September 15, 2006

Prof. Dr. F.R. de Boer