Phonon spectrum and soft-mode behavior of $MgCNi_3$

R. Heid,[1] B. Renker,[1] H. Schober,[2] P. Adelmann,[1] D. Ernst,[1] and K.-P. Bohnen[1]
[1]*Forschungszentrum Karlsruhe, Institut für Festkörperphysik, P.O. Box 3640, D-76021 Karlsruhe, Germany*
[2]*Institut Laue-Langevin, BP 156 X, F-38042 Grenoble Cedex, France*
(Received 24 October 2003; published 26 March 2004)

Temperature-dependent inelastic neutron-scattering measurements of the generalized phonon density-of-states for superconducting $MgCNi_3$, $T_c = 8$ K, give evidence for a soft-mode behavior of low-frequency Ni phonon modes. Results are compared with *ab initio* density-functional calculations. They suggest an incipient lattice instability of the stoichiometric compound with respect to Ni vibrations orthogonal to the Ni-C bond direction which is not directly linked to the superconducting state.

DOI: 10.1103/PhysRevB.69.092511 PACS number(s): 74.25.Kc, 63.20.Kr, 78.70.Nx, 74.70.Dd

The recent discovery of superconductivity near 8 K in $MgCNi_3$ (Ref. 1) was a surprise since due to the high Ni content a ferromagnetic ground state would have been expected rather than a superconducting one. Furthermore it is unusual that for this perovskite compound the heavy Ni atoms occupy the corners in Ni_6C octahedra. There are speculations that magnetic interactions might promote superconductivity,[2] however, measurements of the specific heat come up with the conclusion that $MgCNi_3$ is a medium to strong coupling BCS superconductor.[3,4] This compound bears similarity to superconducting nickel borocarbides where for the Y and Lu compounds an acoustic phonon branch exhibits a pronounced softening at lower temperatures,[5–7] a feature which is supposed to be connected to superconductivity in these compounds. Hints for unusual lattice dynamical properties of $MgCNi_3$ have been inferred from a recent x-ray absorption study, which indicated deviations of the local atomic structure from the ideal perovskite lattice at temperatures below 70 K,[8] and from a very recent linear muffin-tin orbitals (LMTO) calculation of the harmonic phonons of $MgCNi_3$,[9] which found a dynamical instability of the stoichiometric compound. In this paper we will present inelastic neutron scattering (INS) measurements of the generalized phonon density-of-states (GDOS) as a function of temperature which show a softening of low-frequency Ni modes. We will compare our experimental results to *ab initio* density-functional calculations.

For the synthesis of polycrystalline $MgCNi_3$ samples mixed powders of the components were pressed into pellets, wrapped into a tantal foil, sealed in a quartz tube, and heated for 2 h at 900 °C. A difficulty arises from losses of volatile Mg and C at the synthesis temperature. With respect to subsequent x-ray analysis we obtained the best samples for a starting stoichiometry of $Mg_{1.14}C_{1.4}Ni_3$ where an impurity peak due to unreacted graphite was smallest. T_c of our samples was 7.5 K. It could be slightly increased for the starting concentration $C_{1.5}$ however at the expense of a somewhat larger contribution of unreacted graphite. Since the exact stoichiometry might be important for a soft-mode behavior which is found in the present investigation we show in Fig. 1 an x-ray diffraction pattern of our sample taken at room temperature.

Our INS measurements were performed at the HFR in Grenoble, France, on the IN6 and IN4 time-of-flight spectrometers. On IN6 a high chopper speed of 12 060 rpm and focusing in the inelastic region were used to improve the resolution. Due to the low incident energy of 4.75 meV at this spectrometer which is connected to the cold source we profit from a very good resolution for low-energy excitations. The necessity to work in energy gain of the scattered neutrons sets limits on the possibility to work at lower temperatures. For example, for a sample temperature of 50 K we could follow excitations up to ~30 meV. The spectrometer is dedicated to inelastic measurements and a standard result is the GDOS which is calculated from the recorded intensities over a scattering region from 14° to 114°. For the data evaluation we have applied multiphonon corrections in a self-consistent procedure.[10] The GDOS implies a weighting of vibrational modes by σ/m (scattering cross section over the mass; we used values of 0.46, 0.179, and 0.31 b/amu for C, Mg, and Ni, respectively). From a plot of the elastic intensities over momentum transfer we do not obtain any evidence for a structural phase transition within the investigated temperature region in agreement with previous results from structural investigations.[1,11] However, due to the low incident energy this analysis is limited to $Q \leqslant 2.2$ Å^{-1}. To study changes in the dynamics in a larger temperature region, we

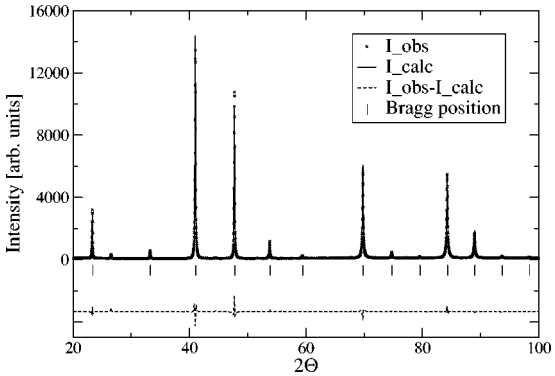

FIG. 1. Observed (crosses) and calculated (solid line) x-ray diffraction pattern for the investigated sample. A small impurity peak at 26.5° is due to unreacted graphite. The refinement ($R = 5\%$) yields a composition of $MgC_{.96}Ni_3$ for the cubic perovskite structure, space group Pm3m, with lattice constant $a = 3.8085(1)$ Å and with positions of the atoms at: Mg 1*a* (0,0,0), C 1*b* (0.5,0.5,0.5), and Ni 3*c* (0,0.5,0.5).

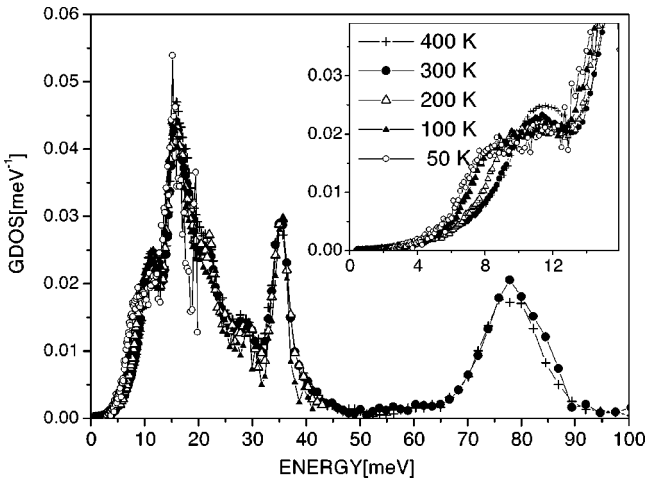

FIG. 2. The experimental generalized phonon density-of-states for $MgCNi_3$. A significant soft-mode behavior is found for low-frequency Ni modes (inset).

have performed supplementary measurements with an incident neutron energy of 35 meV in the down-scattering mode over a wide range of temperatures on the instrument IN4. These results will be presented in the form of the dynamical susceptibility $\chi''(\omega)$ which is obtained by dividing the observed intensities by the thermal population factor. Thus, $\chi''(\omega)$ is much closer related to the scattering function $S(Q,\omega)$ than the GDOS.[10]

Due to the large differences in mass the phonon spectrum of $MgCNi_3$ (Fig. 2) decomposes into two well separated parts, a low-frequency region with predominantly Ni and Mg modes and vibrations of the light C atom around 80 meV. From the known σ/m values and an analysis of the areas in the GDOS shown in Fig. 2 we find for the latter peak an almost perfect agreement between the theoretical and the experimental spectral weight implying contributions from three closely neighbored optical phonon branches. The weight of the sharp and well separated peak at 35 meV corresponds well to the weight expected for three optical Mg modes. It is increased by some 20% which suggests a small hybridization with the low-frequency Ni modes. The region below 33 meV contains exclusively Ni contributions. It is well structured and exhibits a very low-frequency maximum at 12 meV and a strong main peak around 16 meV.

The 12 zone-center optic phonons decompose according to $3F_{1u}+F_{2u}$ with no Raman active modes. Guided by investigations of the related system of quaternary borocarbides where a soft-mode behavior for superconducting $RENi_2B_2C$ (RE=Y, Lu, where RE stands for rare earth) has been found we have measured the GDOS of $MgCNi_3$ for a series of temperatures between 400 K and 50 K. No changes are found for the peaks at 80 meV and 35 meV which were attributed to C and Mg vibrations (only a small sharpening of the 35 meV peak is registered). A pronounced softening, however, occurs for the very low-frequency part of the Ni vibrations in a region which is dominated by acoustic phonon branches. The inset in Fig. 2 shows a magnification. The strongest effect is observed between 200 K and 100 K. Only less pronounced changes occur between 100 K and 50 K

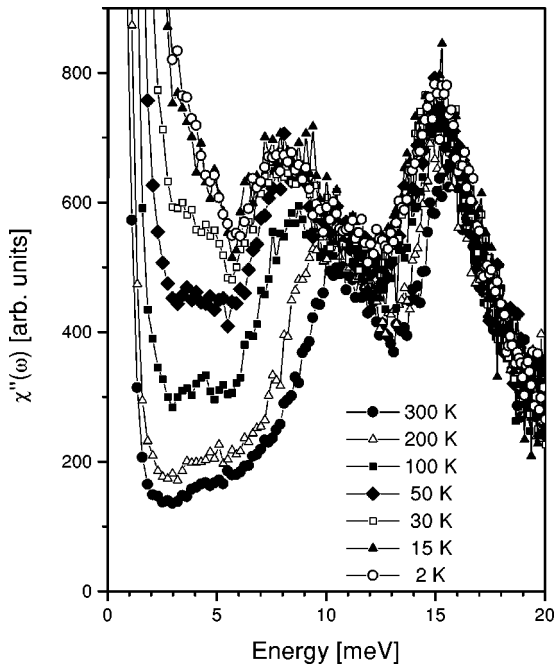

FIG. 3. The experimental dynamical susceptibility for $MgCNi_3$ (see text).

which is the lowest temperature in our energy-gain measurements.

Changes in the dynamics can be seen easier in the temperature evolution of $\chi''(\omega)$ in Fig. 3 where a sum of intensities recorded for different scattering angles on IN4 is shown. The softening of the low-frequency Ni peak shows up clearly, and becomes less pronounced below 100 K. No significant changes are observed between 2 K and 15 K. The strong intensity increase below 3 meV is caused by the finite instrumental resolution and a very strong elastic scattering component. Whereas the frequency of the prominent Ni peak remains almost fixed at 16 meV we can observe the evolution of the soft-mode intensity. In agreement with the GDOS the strongest changes are observed around 100 K and only minor changes are recorded between 300 K and 200 K and between 30 K and 2 K. Additionally to the GDOS in Fig. 2 it can be seen that some intensity is shifted into the low-frequency region below 5 meV. While the increase in intensity below 10 meV is in general agreement with the mode softening a more detailed analysis of its location within the Brillouin zone (BZ) is not possible for this polycrystalline sample.

For an analysis of our data we have performed first-principles density-functional calculations using a mixed-basis pseudopotential method. For Mg a well tested pseudopotential of Troullier-Martins type has been used,[12,13] whereas for C and Ni Bachelet-Hamann-Schlüter type pseudopotentials were constructed.[14] The fairly deep *d* potential of Ni and *p* potential of C can be efficiently dealt with by the mixed-basis formalism, where the valence states are constructed from a combination of localized *s* and *p* functions at C sites and localized *d* functions at Ni sites, supplemented by plane waves up to a kinetic energy of 24 Ry. The local-density approximation with the Hedin-Lundqvist pa-

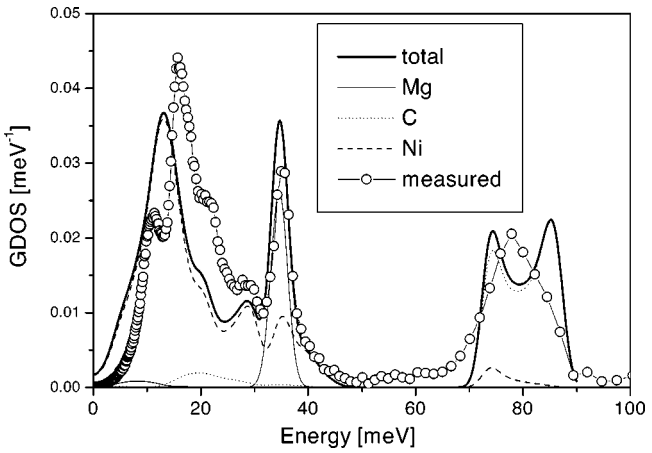

FIG. 4. Calculated GDOS spectra for stoichiometric $MgCNi_3$. The proper σ/m values have been applied for a comparison to the experimental data (300 K spectrum). Contributions from an unstable phonon branch (see text) have been ignored.

rametrization of the exchange-correlation functional[15] has been used. Our calculated electronic band structure is in good agreement with previous density-functional studies.[2,16–22] The most prominent feature of the electronic density-of-states is the existence of a strong and sharp van Hove peak less than 100 meV below E_F. It arises from antibonding bands related to the Ni *d* orbitals, which are very narrow due the linear Ni coordination by C.[19]

Phonon-dispersion curves for stoichiometric $MgCNi_3$ were calculated within the mixed-basis perturbation approach.[23] Complete spectra are obtained from a Fourier interpolation of dynamical matrices calculated on a cubic $(4\times4\times4)$ *q*-point mesh. Results for the optimized lattice constant $a=3.76$ Å are depicted in Figs. 4 and 5. The theoretical GDOS (Fig. 4) reproduces many features seen in the experimental spectra, including the small maximum near 30 meV and the shoulder of the acoustic spectrum at 20 meV.

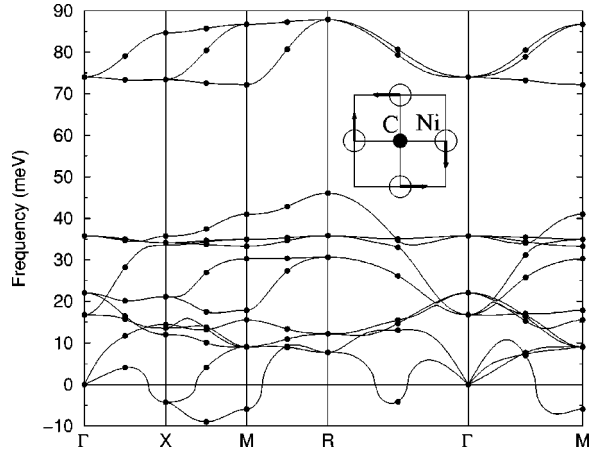

FIG. 5. Calculated phonon-dispersion curves for stoichiometric $MgCNi_3$ for selected symmetry directions. Black circles denote the results from linear-response calculations. Lines are obtained by Fourier interpolation. Negative frequencies indicate unstable modes. At the *M* point, the unstable phonon corresponds to shear elongations of Ni atoms in the Ni-C planes as indicated in the inset.

The acoustic modes are predominantly of Ni character with only a small hybridization of C modes. The sharp peak near 35 meV arises from three almost dispersionless Mg branches with a small admixture of Ni vibrations.

The most prominent feature of the calculated dispersion curves (Fig. 5) is, however, the occurrence of unstable modes suggesting that the stoichiometric compound is dynamically unstable in the harmonic approximation. This instability appears over a large area in reciprocal space and is most pronounced near the zone boundary points *X* and *M* (with coordinates (100) and (110) in units of π/a, respectively). Inspection of the displacement vectors reveals that all unstable modes involve Ni vibrations orthogonal to the Ni-C bond directions. This behavior is most evident at the *M* point where the unstable mode represents a pure vibration of the Ni atoms with all other atoms at rest. Its elongation pattern, shown in the inset of Fig. 5, induces shear distortions in the planar Ni-C sublattice. This extended phonon instability may be the origin of the apparent downshift of the acoustic part below 20 meV in the calculated spectrum by 3 meV with respect to the experimental one (see Fig. 4).

The presence of the van Hove peak close to E_F requires care in performing the BZ summations in the calculations. The presented results were obtained with cubic $(16\times16\times16)$ Monkhorst Pack *k*-point meshes and a Gaussian broadening of 0.1 eV. Convergence studies showed that this is sufficient for most of the phonon modes to be converged within 0.5 meV, but the low-frequency Ni modes are more sensitive to the BZ sampling. Frozen-phonon studies of the unstable *M*-point mode using a variety of *k* meshes and Gaussian smearings have confirmed that this instability is not the result of an insufficient BZ sampling. Furthermore, a similar frozen-phonon calculation performed with the projector-augmented plane wave approach as implemented in the Vienna *ab initio* simulation package (VASP-PAW) (Refs. 24–27) reproduced the instability, excluding the possibility that it is an artefact of the pseudopotential approximation.

An instability of Ni modes has been also found in a very recent *ab initio* investigation of the lattice dynamics and electron-phonon coupling (EPC) of $MgCNi_3$ using the LMTO method.[9] In contrast to our calculations, however, the instability did not appear at high-symmetry points at the BZ boundary. While both methods agree with respect to the frequency range for the Ni and C modes, the LMTO calculations predict significantly higher frequencies for the Mg modes (at ≈45 meV) at variance with our experimental and theoretical results.

The instability of the harmonic lattice dynamics of stoichiometric $MgCNi_3$ raises the question of the true low-temperature structure of this superconductor. Some insight can be gained from frozen-phonon studies for the unstable mode. For the shear mode at *M* we found a very shallow double-well potential, with a minimum of less than 1 meV at a displacement of only 0.025 Å. In the previous LMTO study, double-well potentials of similar magnitude have been extracted from frozen-phonon calculations corresponding to lower-symmetry points.[9] The shallowness of the double well suggests that the instability is not strong enough to induce a long-ranged structural distortion, but that the high-symmetry

cubic structure is stabilized dynamically. The presence of strong anharmonic motions of atoms in the vicinity of a structural instability could be of relevance for superconductivity, as it may significantly enhance the EPC strength. For $MgCNi_3$, a contribution of 37% coming from the anharmonic modes to the total EPC constant has been estimated on the basis of the LMTO results.[9] A complete calculation of the EPC strength, however, is a formidable task as it requires to take into account the full anharmonic lattice dynamics as well as anharmonic corrections to the EPC. This is further complicated by the fact that the local distortions are expected to strongly modify the van Hove singularity and thus the electronic structure in the vicinity of the Fermi energy.[9]

The picture of a dynamically stabilized cubic structure is consistent with published structural investigations where no indications of any phase transition have been found,[1,11] and with the temperature dependence of the elastic-scattering intensity observed in our IN6 spectra. In a recent x-ray absorption fine structure measurement, an unusually broad Ni-Ni pair-correlation function has been observed below 70 K.[8] It was interpreted as the result of local distortions of the Ni octahedra predominantly perpendicular to the Ni-C bond with displacements of less than 0.05 Å, in agreement with the frozen-phonon results. Such distortions would be too small to be observable in diffraction experiments.

In conclusion, studies of the GDOS have provided a clear insight in the lattice vibrations of superconducting $MgCNi_3$ which can be looked at as a three-dimension analogue of the nickel borocarbides. For both kinds of compounds a remarkable soft-mode behavior in the low-frequency region ($\sim$8 meV) is observed. For the superconducting borocarbides where single crystals could be grown it was shown that the mode softening is restricted to a narrow region in reciprocal space and is sensitive to the formation of the superconducting gap.[7] In contrast, the present results suggest that the softening phenomena in $MgCNi_3$ is not directly linked to the superconducting state, but has its origin in an incipient dynamical instability of specific Ni vibrations which occurs widespread in reciprocal space. It cannot be excluded, however, that lattice defects play an important role in stabilizing the real structure. Further studies are required to clarify the question whether the apparently large stability range of the $MgC_{1-x}Ni_3$ phase is connected to the observed dynamical peculiarities.

[1] T. He, Q. Huang, A.P. Ramirez, Y. Wang, K.A. Regan, N. Rogado, M.A. Hayward, M.K. Haas, J.S. Slusky, K. Inumaru, H.W. Zandbergen, N.P. Ong, and R.J. Cava, Nature (London) **411**, 54 (2001).

[2] H. Rosner, R. Weht, M.D. Johannes, W.E. Pickett, and E. Tosatti, Phys. Rev. Lett. **88**, 027001 (2002).

[3] J.-Y. Lin, P.L. Ho, H.L. Huang, P.H. Lin, Y.-L. Zhang, R.-C. Yu, C.-Q. Jin, and H.D. Yang, Phys. Rev. B **67**, 052501 (2003).

[4] J.-Y. Lin and H.D. Yang, cond-mat/0308198 (unpublished).

[5] P. Dervenagas, M. Bullock, J. Zarestky, P. Canfield, B.K. Cho, B. Harmon, A.I. Goldman, and C. Stassis, Phys. Rev. B **52**, R9839 (1995).

[6] F. Gompf, W. Reichardt, H. Schober, B. Renker, and M. Buchgeister, Phys. Rev. B **55**, 9058 (1997).

[7] J. Zarestky, C. Stassis, A. Goldman, P. Canfield, G. Shirane, and S. Shapiro, Phys. Rev. B **60**, 11 932 (1999).

[8] A.Yu. Ignatov, L.M. Dieng, T.A. Tyson, T. He, and R.J. Cava, Phys. Rev. B **67**, 064509 (2003).

[9] A. Ignatov, S.Y. Savrasov, and T.A. Tyson, Phys. Rev. B **68**, 220504 (2003).

[10] H. Schober, A. Tölle, B. Renker, R. Heid, and F. Gompf, Phys. Rev. B **56**, 5937 (1997).

[11] Q. Huang, T. He, K.A. Regan, N. Rogado, M.A. Hayward, M.K. Haas, K. Inumaru, and R.J. Cava, Physica C **363**, 215 (2001).

[12] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).

[13] G. Pelg, Ph.D. thesis, Universität Regensburg, 1996.

[14] G.B. Bachelet, D.R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[15] L. Hedin and B.I. Lundqvist, J. Phys. C **4**, 2064 (1971).

[16] M.A. Hayward, M.K. Haas, A.P. Ramirez, T. He, K.A. Regan, N. Rogado, K. Inumaru, and R.J. Cava, Solid State Commun. **119**, 491 (2001).

[17] A. Szajek, J. Phys.: Condens. Matter **13**, L595 (2001).

[18] S.B. Dugdale and T. Jarlborg, Phys. Rev. B **64**, 100508 (2001).

[19] D.J. Singh and I.I. Mazin, Phys. Rev. B **64**, 140507 (2001).

[20] J.H. Shim, S.K. Kwon, and B.I. Min, Phys. Rev. B **64**, 180510 (2001).

[21] I.G. Kim, J.I. Lee, and A.J. Freeman, Phys. Rev. B **65**, 064525 (2002).

[22] I.R. Shein, A.L. Ivanovskii, and N.I. Medvedeva, JETP Lett. **74**, 122 (2001).

[23] R. Heid and K.-P. Bohnen, Phys. Rev. B **60**, R3709 (1999).

[24] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); **49**, 14 251 (1994).

[25] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[26] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).

[27] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).