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FINAL REPORT ON CALIFORNIA INSTITUTE OF TECHNOLOGY JET PROPULSION LABORATORY CONTRACT #955734

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for

Performing Spectroscopic and Specific Heat Studies of Improper Ferroelectrics

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(NASA-CR-169204) PERFORMING SPECTROSCOPIC AND SPECIFIC HEAT STUDIES OF IMPROPER FERROELECTRICS Final Report (California Univ.) 17 p HC A02/MF A01 CSCL 07D
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Introduction

This contract originally called for spectroscopic and specific heat studies of improper ferroelectrics, the samples to be provided by JPL. Insufficient material was received to perform specific heat measurements, however much new and exciting information on the Boracite improper ferroelectrics was obtained from infrared (4000-400 cm^{-1}) and far infrared (10-400 cm^{-1}) reflectance spectroscopy. This report contains the results of infrared measurements on Ni-Br, Cu-Cℓ, and Fe-I Boracite and far infrared measurements of Ni-Br Boracite.

The Boracites have the general formula $X_3B_7O_3Y$, where X = divalent metal and Y = halogen. They undergo a first order phase transition from a high temperature paraelectric phase with cubic symmetry to a ferroelectric phase with orthorhombic symmetry. The Boracites are "improper ferroelectrics" since the spontaneous polarization is not the primary order parameter in the cubic-orthorhombic phase transition. Current understanding of these materials is that the primary order parameter is associated with a doubly degenerate zone-boundary phonon in the cubic phase. The degenerate critical modes become homogeneous and split into the A_1 and A_2 modes in the orthorhombic phase, doubling the volume of the primitive cell. An harmonic coupling between the softing A_1 mode and a low frequency A_1 optic mode induces a spontaneous polarization as a secondary effect in the ferroelectric phase. This secondary non-critical nature of the ferroelectric mode earns these materials the "improper" title and is responsible for their unique properties and high figure of merit in detector use.

Infrared Results

We have measured the unpolarized infrared reflectance of unoriented Cu-Cℓ, Fe-I, and Ni-Br Boracite crystals, and the polarized reflectivity of Ni-Br Boracite with $\vec{E}\,||\,\hat{c}$ and $E\perp\hat{c}$ ($\hat{c}$ is the ferroelectric axis). A Nicolet MX-1 fourier transform spectrometer was used, covering the region from 4000-400 cm^{-1}. The unpolarized reflectivities of all three Boracites are very similar and that of Fe-I boracite is shown in figure 1. The room temperature polarized reflectivity spectra of Ni-Br Boracite are shown in figures 2a-b. The reflectivity in all cases is featureless from 1500-4000 cm^{-1} and all display primarily the internal modes of the B-O network from 1400 to 400 cm^{-1}. The polarized reflectance from Ni-Br Boracite displays, splitting of several modes in the $E\,||\,\hat{c}$ spectrum versus $E\perp\hat{c}$. The $E\,||\,\hat{c}$ spectrum contains modes at 1159 cm^{-1}, 1065 cm^{-1}, 972 cm^{-1} at 950 cm^{-1} not seen with $\vec{E}\perp\hat{c}$.

The spectra were measured at elevated temperatures though the ferroelectric-paraelectric phase transition. Of particular interest is the B-O_3 stretching mode near 1430 cm^{-1}. In all three materials the intensity of this mode drops monotonically as T_c is approached and then drops sharply at T_c. Above T_c its intensity remains small and constant. The temperature dependence of the B-O_3 stretch for all three materials is shown in figure 3.

In the X-ray crystallographic study of Mg-Cℓ Boracite by Dorvoty and Clark the displacement of the boron and oxygen atoms in the orthorhombic phase was found to be comparable to those of the metal and halogen ions. Thus our observation of intensity changes in the B-O_3 stretching mode at T_c would indicate a similar behavior in these materials. In addition the precipitous drop in intensity could be interpreted as indicating that the boron-oxygen network is responsible for the displacement of the metal-halogen sublattice and not vice-versa.

Far Infrared Results

The unpolarized reflectance of a single crystal sample of Ni-Br Boracite was measured in the far infrared using a Beckman (RIIC) FS720 Michelson Interferometer, modified with a discrete stepping drive. A gallium doped germanium bolometer operated near 1.3°K was used to detect the far IR radiation. Our preliminary results show strong modes near 130 cm^{-1} and 280 cm^{-1}, figure 4. We have followed the mode near 130 cm^{-1} from 4°K to above the transition, figures 5a-f. As the temperature is raised the mode softens slightly and dampens considerably. Above the ferrolectric-paraeletric transition the mode has dampened (or disappeared) completely.

Conclusions

Our study of the infrared and far infrared response of Ni-Br, Cu-Cℓ and Fe-I Boracite has produced a wealth of information on these materials. The results of the studies made to date indicate that the boron-oxygen framework may be the active agent in the improper ferroelectric transition, driving the dipolar mode (metal-halogen). In the far infrared, study of the mode at 130 cm^{-1} as well as lower frequency modes may help us elucidate the mechanics of the improper ferroelectric phase transition and

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the form of the coupling between the non-polar primary critical mode and the dipolar ferroelectric mode.

Future Plans

We are continuing our far infrared study of Ni-Br Boracite. An improved reflectance apparatus operating above room temperature has completed preliminary check out. It is planned to perform both unpolarized and polarized reflectance measurements on Ni-Br Boracite from room temperature to above the ferroelectric transition. The usual problem of insufficient samples continues to plague the project. The difficulties in growing and cutting oriented Boracite samples, along with domain problems makes this system difficult to study. It is hoped that work will continue in producing oriented crystals of the propionate family where aqueous crystal growth ease the problems. We plan to continue to study the infrared and far infrared response improper ferroelectrics. Combined with the Raman studies now underway at JPL, these measurements should produce the first picture of the lattice dynamics involved in the improper ferroelectric phase transition.

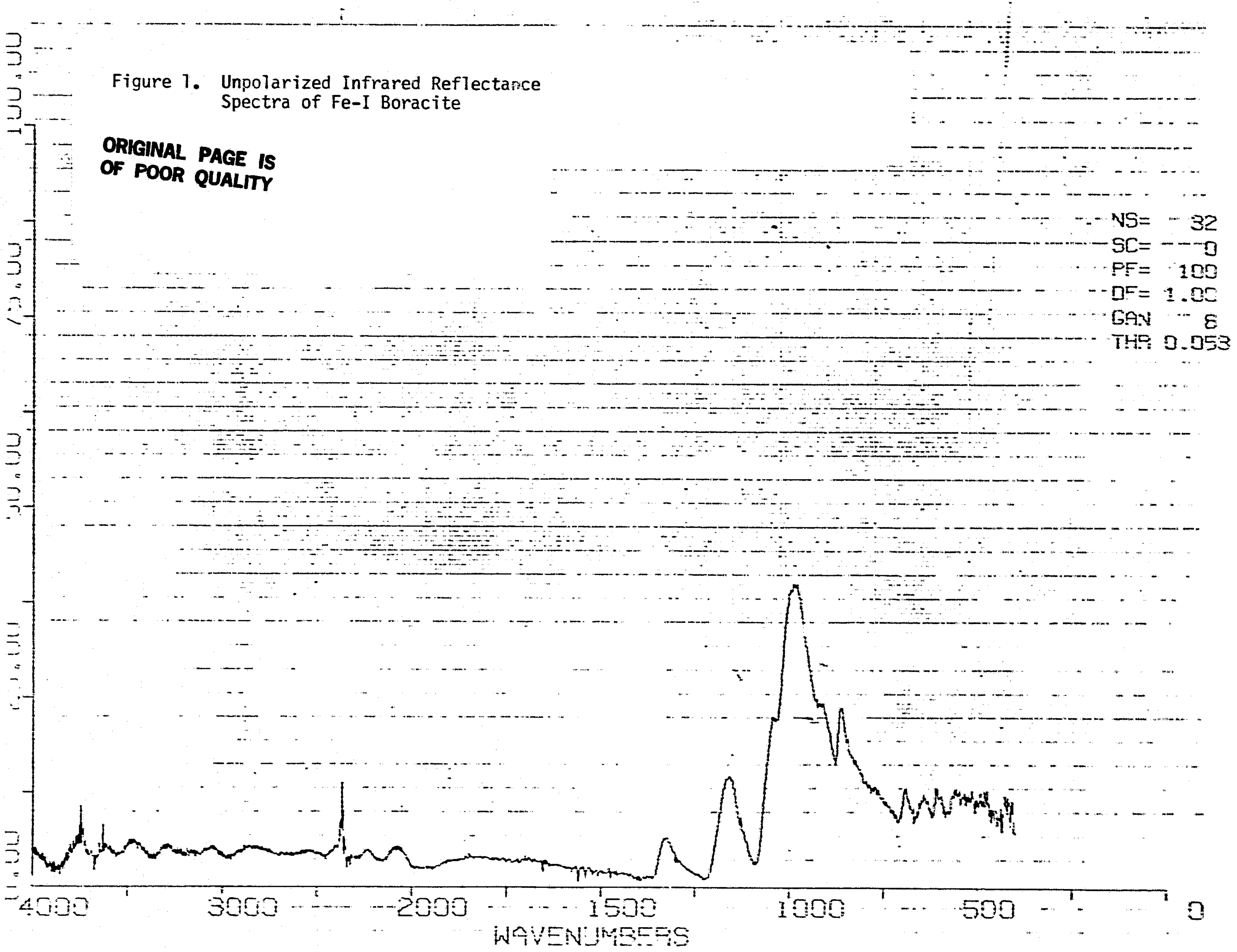

Figure 1. Unpolarized Infrared Reflectance Spectra of Fe-I Boracite

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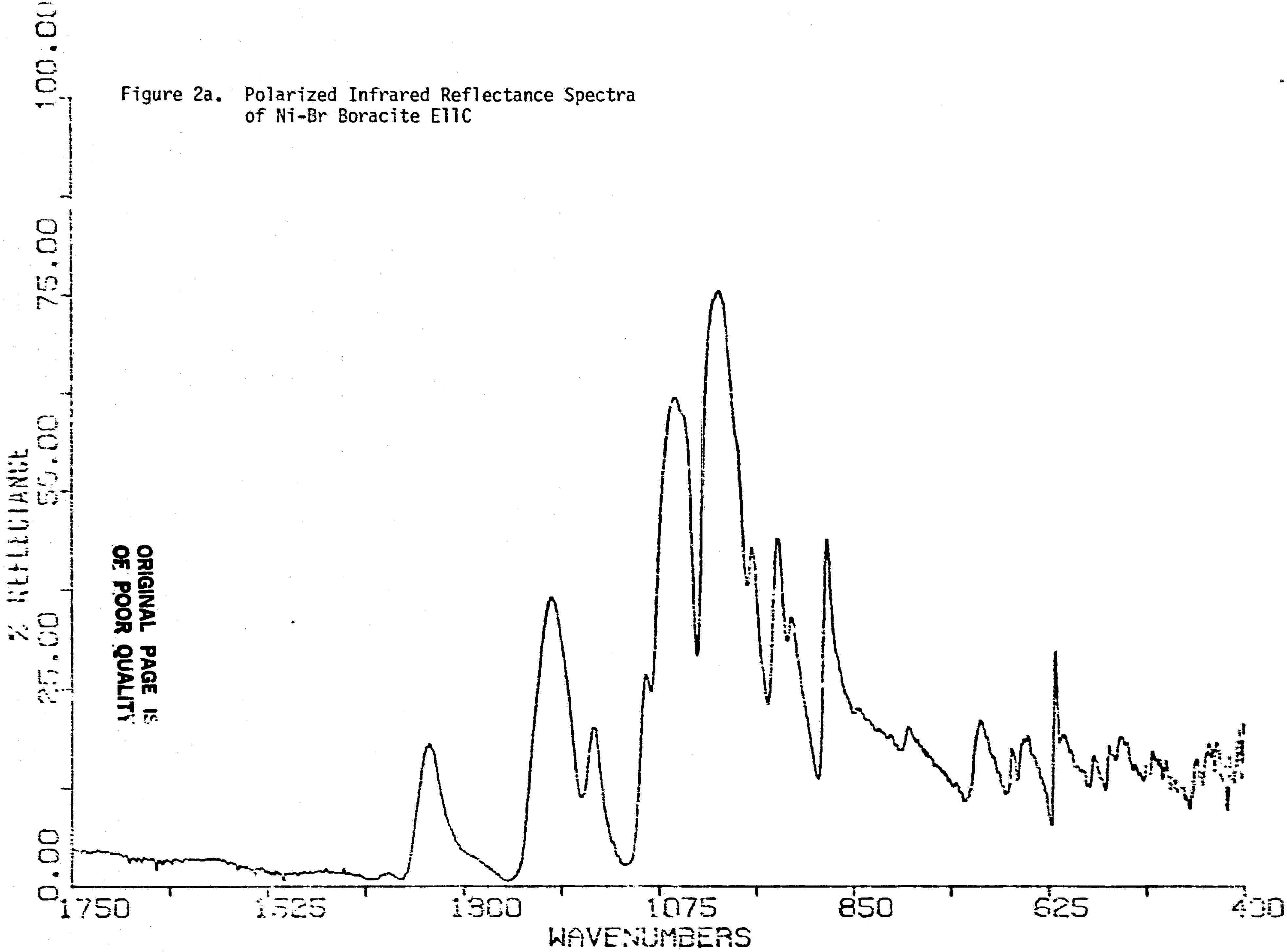

Figure 2a. Polarized Infrared Reflectance Spectra of Ni-Br Boracite E11C

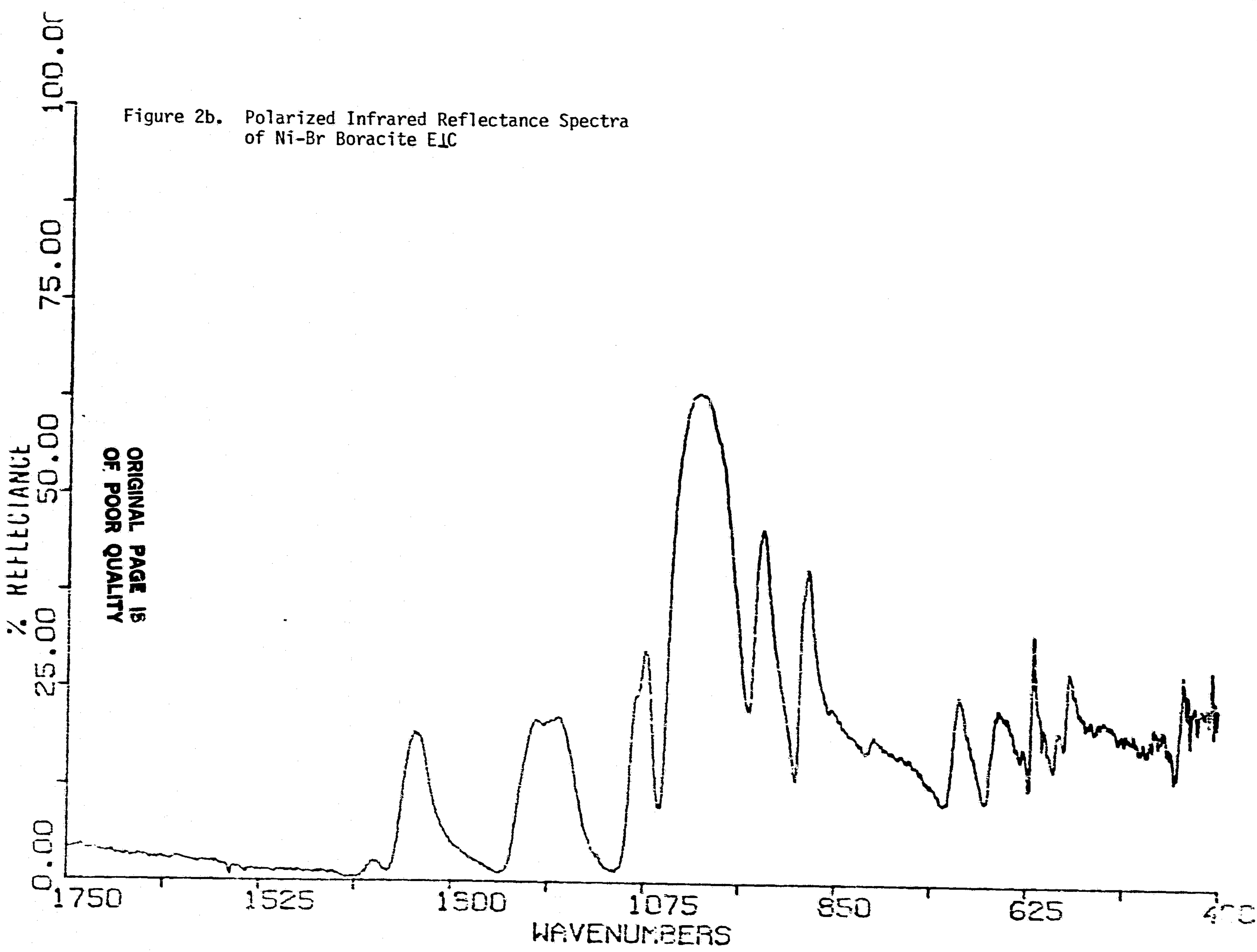

Figure 2b. Polarized Infrared Reflectance Spectra of Ni-Br Boracite E⊥C

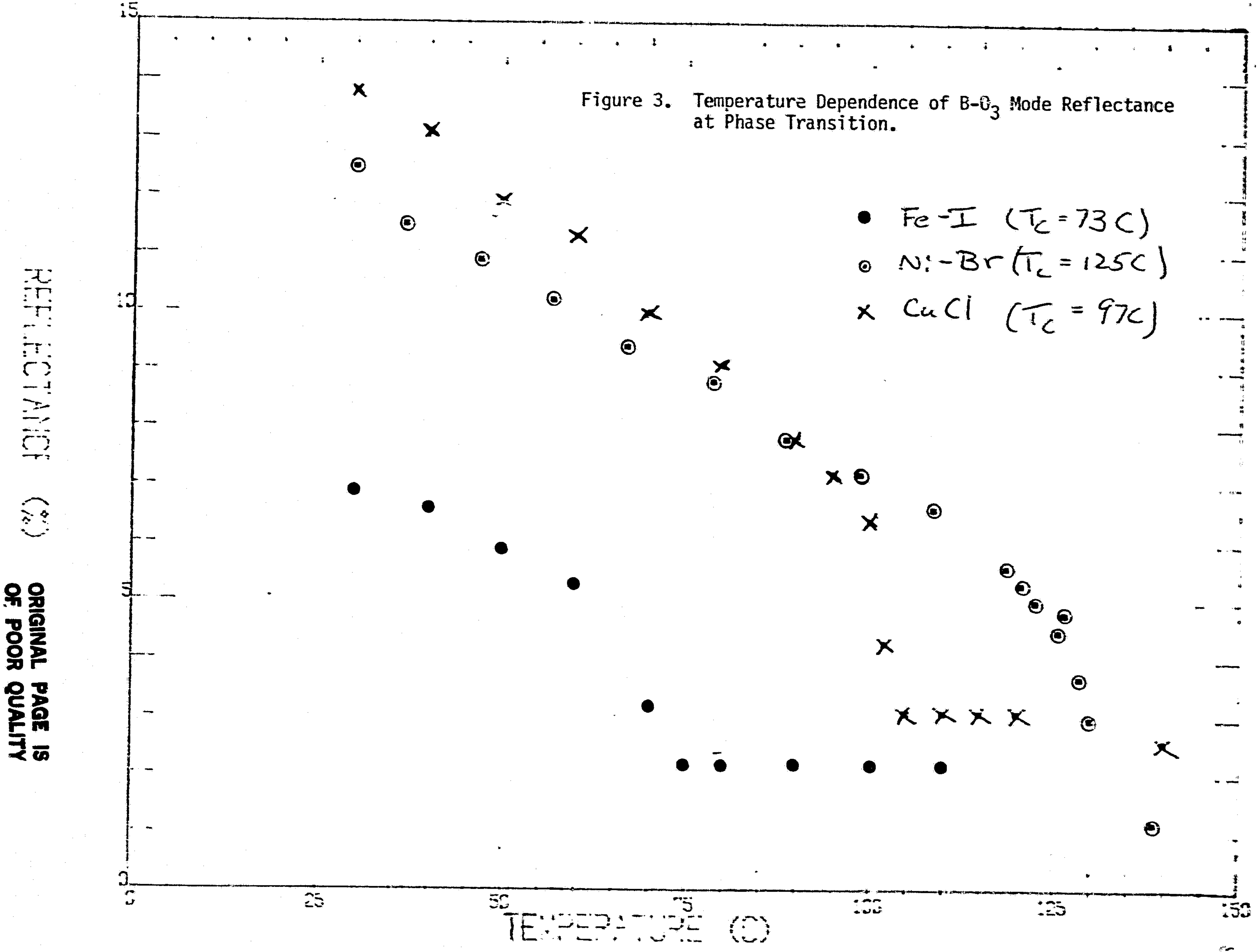

Figure 3. Temperature Dependence of B-O$_3$ Mode Reflectance at Phase Transition.

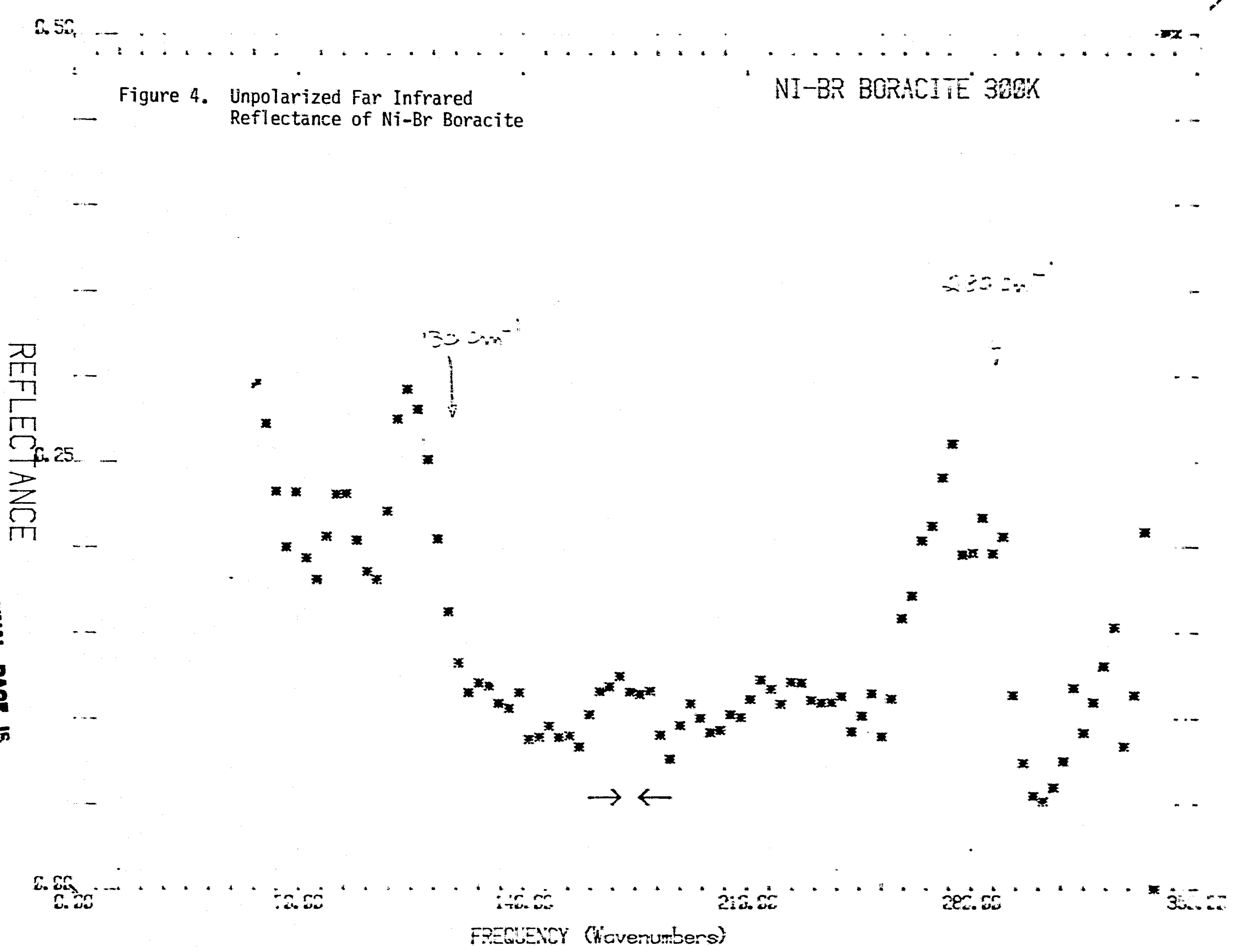

Figure 4. Unpolarized Far Infrared Reflectance of Ni-Br Boracite

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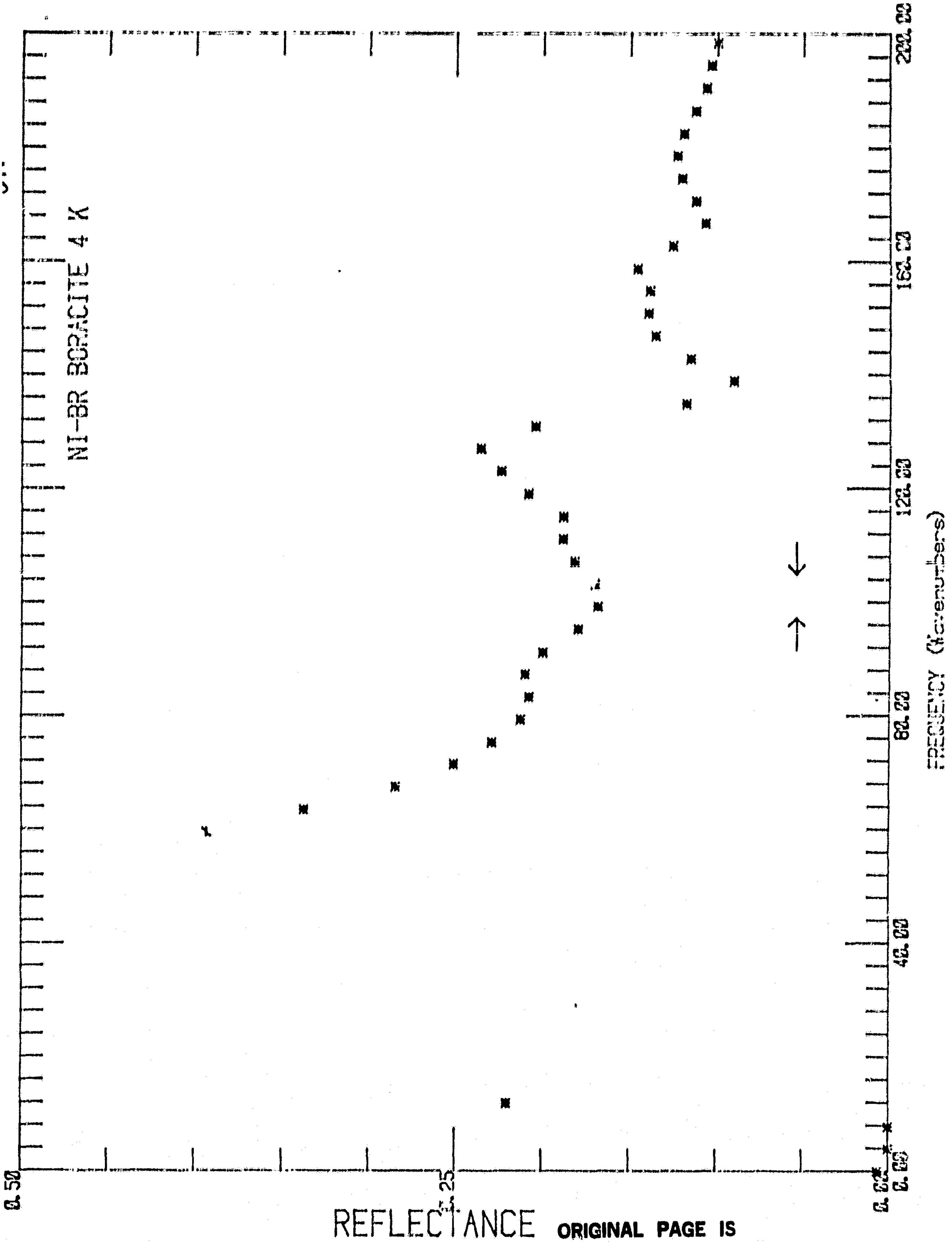
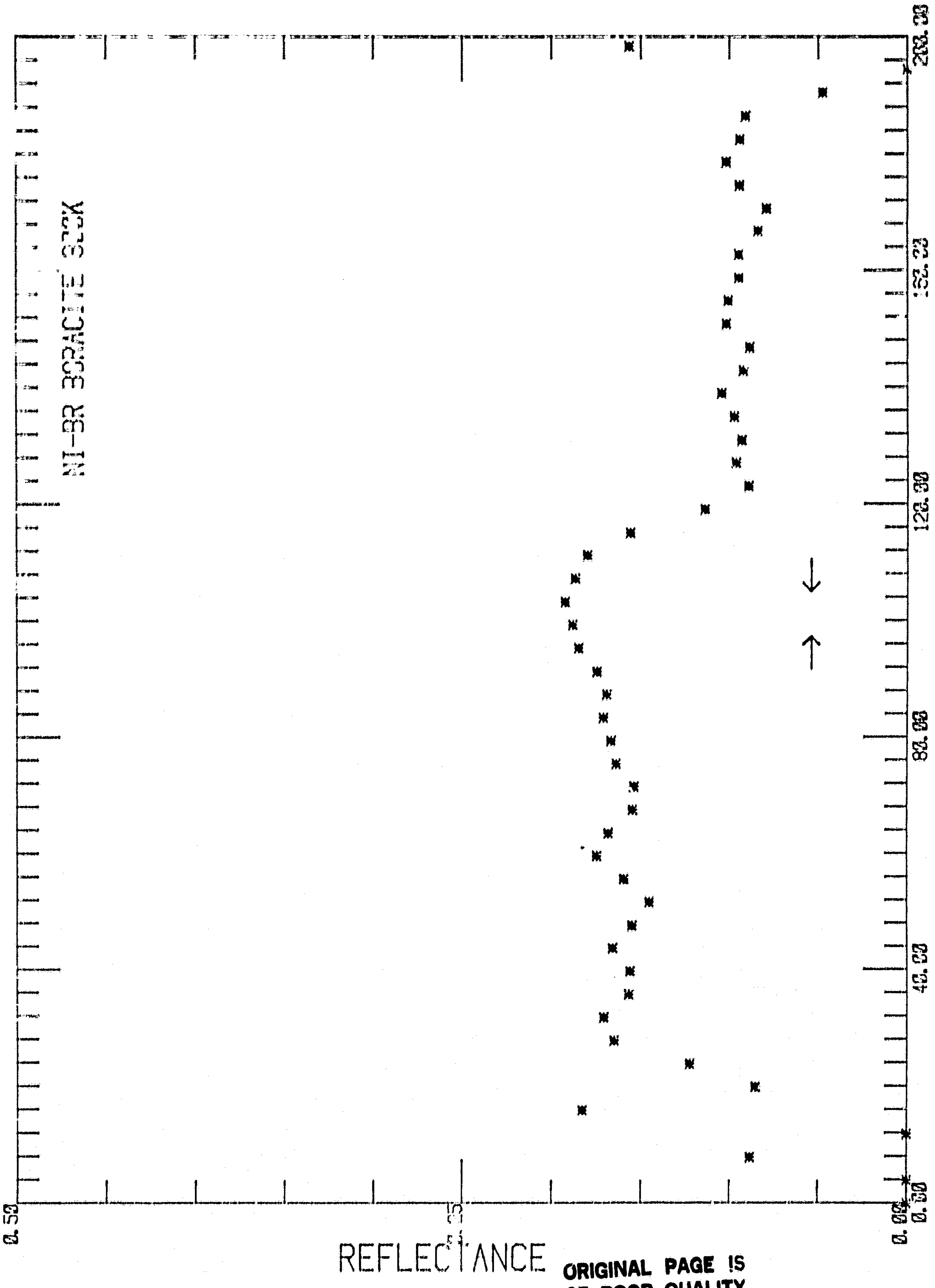
Figure 5. Unpolarized Far Infrared Reflectance of Ni-Br Boracite

a - 4 °K
b - 300 °K - Room Temperature
c - 373 °K - 100 °C
d - 393 °K - 120 °C
e - 403 °K - 130 °C
f - 438 °K - 165 °C


NI-BR BORACITE 4 K
FREQUENCY (Wavenumbers)
0.00
40.00
80.00
120.00
160.00
200.00
REFLECTANCE
0.50
0.25
0.00



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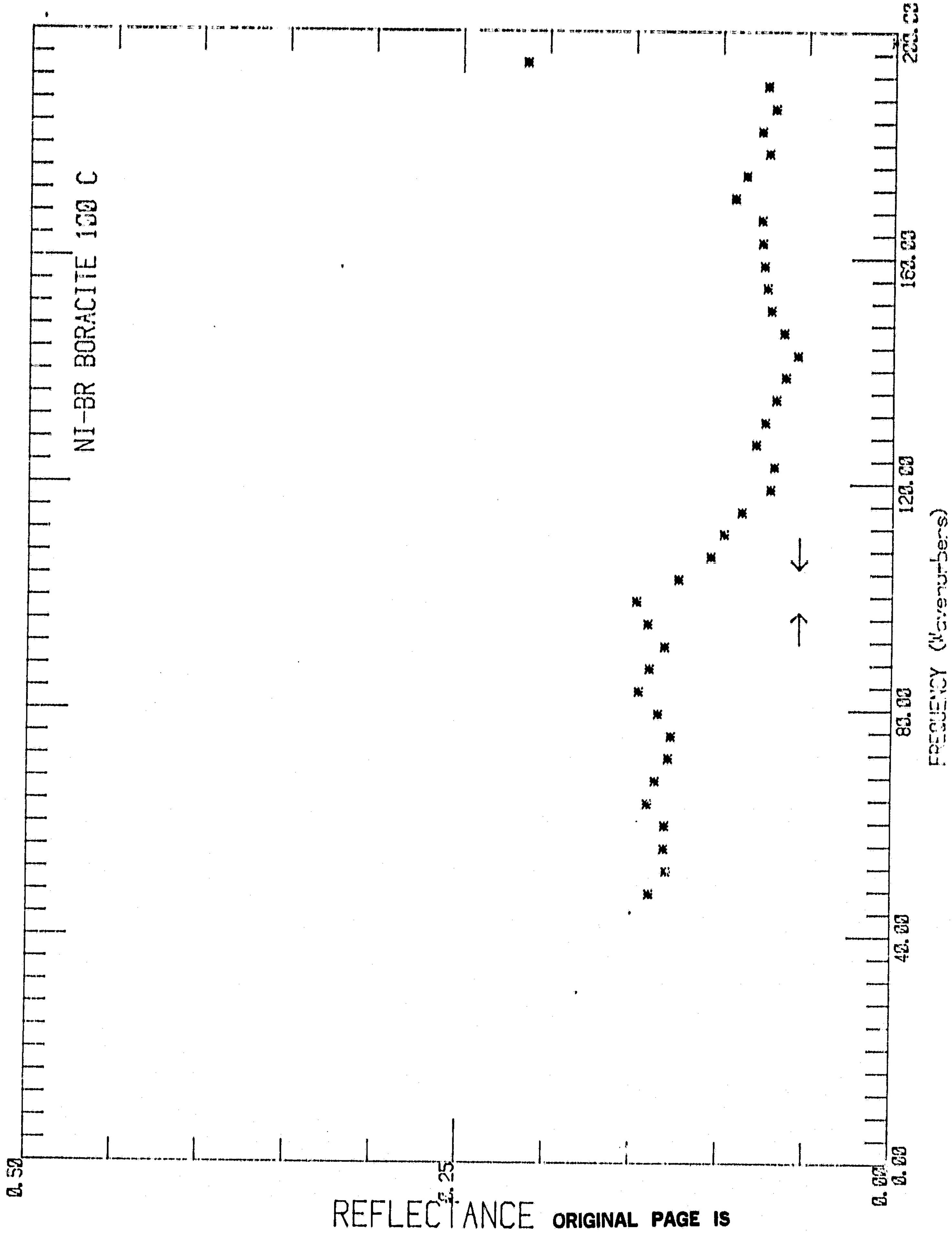

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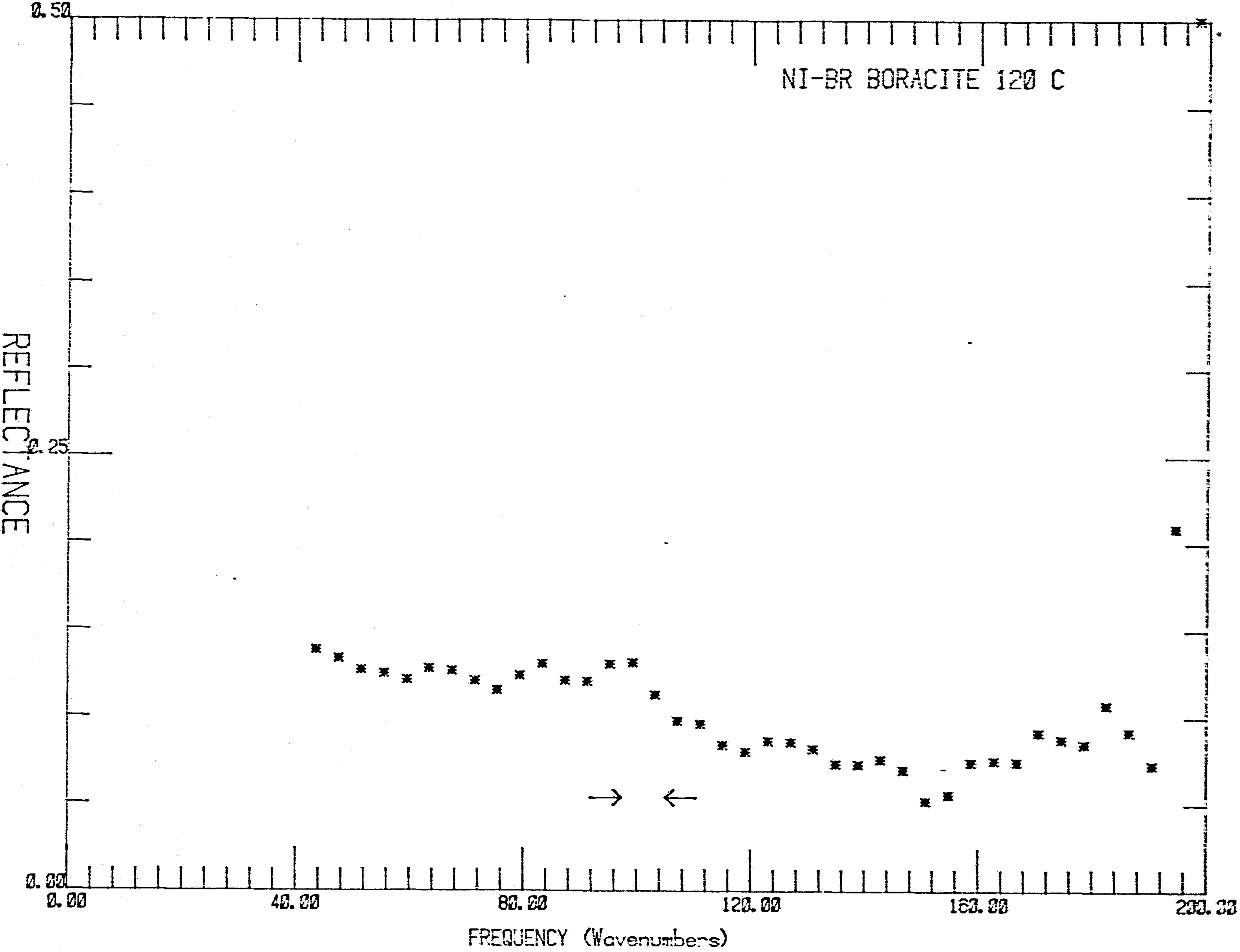

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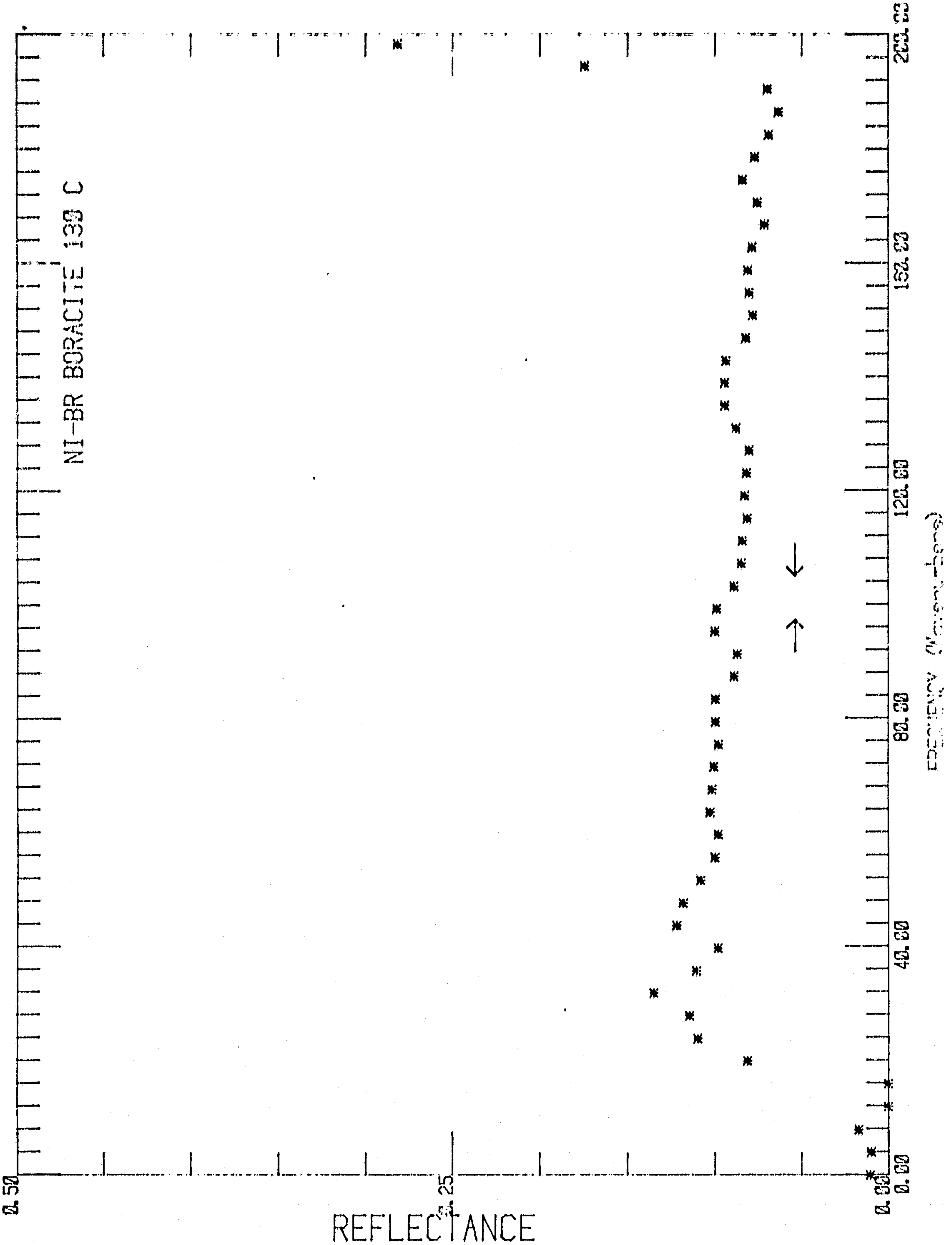

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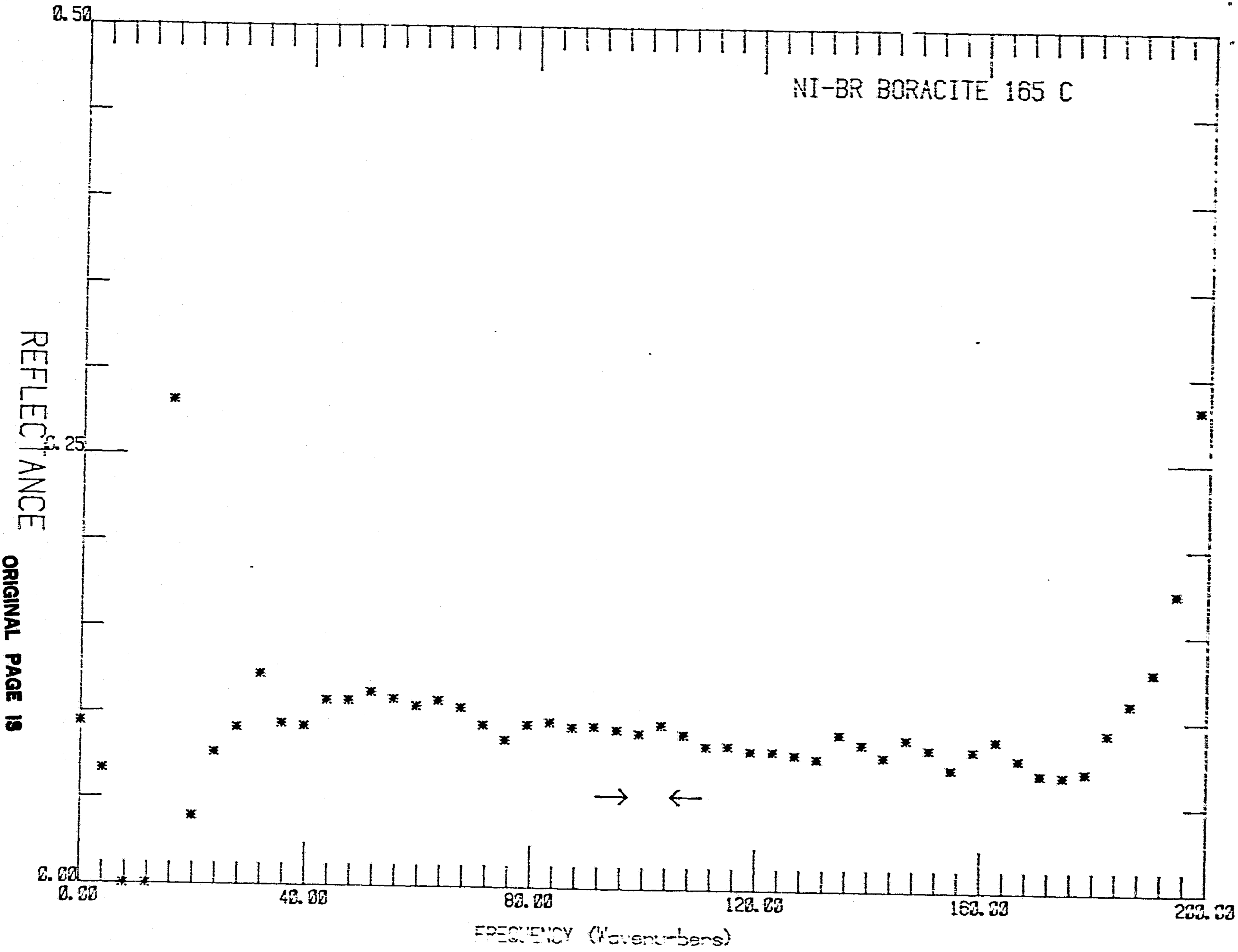NI-BR BORACITE 165 C
REFLECTANCE
0.50
0.25
0.00
0.00
40.00
80.00
120.00
160.00
200.00
FREQUENCY (Wavenumbers)